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THE ATOMIC WEIGHT OF MAGNESIUM AS DETERMINED BY THE COMPOSITION OF ITS OXIDE.

BY W. M. BURTON AND L. D. VORCE.

The method employed by Dr. H. N. Morse¹ and one of us (B) for the preparation of pure zinc and the determination of its atomic weight yielded such satisfactory results that it seemed desirable to employ the same process for the purification of other metals and for the redetermination of their atomic weights. Among others, magnesium was suggested as being suitable for the purpose because, like zinc, it can be distilled at a comparatively low temperature, and its nitrate, upon ignition, yields an oxide of definite composition, and stable when heated to a very high temperature.

Therefore, in accordance with an understanding with Dr. Morse, we have undertaken the redetermination of its atomic weight. Several investigators have determined the atomic weight of magnesium, but in almost every instance either some impurity was found to exist in the materials used, or else some defect was discovered in the method employed, thereby creating doubt as to the accuracy of the results obtained. The following methods have been used:

1. Composition of sulphate by action of sulphuric acid on the oxide (Berzelius,² Bahr,³ Svanberg and Nordenfeldt,⁴ and Magnac⁵).

¹ This Journal 10, 311.

² Pogg. Ann. 8, 188.

³ Jour. f. pr. Ch. 56, 310.

⁴ Ibid. 45, 474.

⁵ Ann. ch. phys. (6) 1, 321.

2. Determination of sulphuric acid in the sulphate by precipitation as barium sulphate (Scheerer,¹ Jacquelain,² and Gay-Lussac³).
3. Conversion of oxalate into oxide by ignition (Svanberg and Nordenfeldt⁴).
4. Conversion of sulphate into oxide by ignition (Gay-Lussac⁵).
5. Determination of chlorine in magnesium chloride (Dumas⁶).
6. Conversion of carbonate into oxide by ignition (Marchand and Scheerer⁷).

The results of these investigations are shown in the following table:

Date.	Investigators.	At. wt. Mg (O = 16).	At. wt. Mg (O = 15.95).
1819	Gay-Lussac	22.89	22.812
1820	"	24.18	24.102
1826	Berzelius	25.20	25.122
1846	Scheerer	24.11	24.032
1847	{ Svanberg Nordenfeldt	24.63	24.562
1850	Jacquelain	24.11	24.032
1850	{ Marchand Scheerer	23.96	23.882
1852	Bahr	24.74	24.662
1859	Dumas	24.48	24.502
1884	Marignac	24.38	24.302

The method which we propose is essentially the same as that which was used in the determination of the atomic weight of zinc, and previously described in this Journal.⁸ Slight changes have been made in some details of the manipulation, and these will be noted in their appropriate places. The magnesium was purified by distillation in a vacuum. Weighed portions of the metal were converted into the nitrate, which was ignited to the oxide, first in a hot-air bath, and finally at the highest temperature obtainable in a muffle furnace. The simplicity and directness of the method are strong points in its favor, and we believe we have eliminated the two general difficulties by which the accurate determination of the atomic weight of magnesium has been beset, viz. first, presence of impurities in the materials used; second, the error involved in determining these impurities and correcting for them.

¹ Pogg. Ann. **69**, 535.

² Ann. ch. phys. (3) **32**, 202.

³ Ibid. (2) **13**, 308.

⁴ Jour. f. pr. Ch. **45**, 474.

⁵ Loc. cit.

⁶ Ann. ch. phys. (3) **55**, 189.

⁷ Jour. f. pr. Ch. **50**, 385.

⁸ Loc. cit.

I. The Preparation of Pure Magnesium.

When an attempt was made to distill the magnesium in ordinary hard glass tubes, it was found that the vapors of the metal attacked the glass, forming a black voluminous substance which evolved a spontaneously inflammable gas when treated with an acid. The action of magnesium powder on silica and other oxides has been studied by Gattermann,¹ and his results lead us to conclude that the black substance which we obtained was magnesium silicide of the formula Mg_2Si , and the explosive gas was undoubtedly silicon tetrahydride. Further, when the silicide was dissolved in acid there remained a yellow substance which probably was the suboxide of silicon described by Mabery.² Repeated fractional distillation did not entirely separate this silicide of magnesium from the pure metal. In consideration of the fact that magnesium forms no alloys with iron, the idea suggested itself of using an iron tube inside the glass tube. Fig. 1 represents the

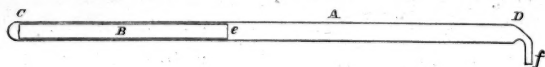


FIG. 1.

method of arrangement. *A* is a tube of hardest potassa glass, fused together at one end. *B* is tube made of thin sheet iron of the best quality obtainable. The iron tube was pushed into the glass tube as represented and then filled with small pieces of magnesium ribbon. The end of the iron tube at *e* is bent over in such a way as to prevent the carrying over of small pieces of magnesium during the distillation. About ten grams of the metal were used in each charge. The glass tube was connected at *f* with a Sprengel air-pump and the apparatus thoroughly exhausted. The tube was heated in a combustion furnace throughout its whole length, but most strongly at *B*. When the iron tube showed a bright red heat the magnesium commenced to volatilise and sublime on the cooler portions of the tube at *A*, forming at first a black mirror of magnesium silicide.

Our first plan was to use an iron tube extending from *C* to *D*, so that the glass would be entirely protected from the vapors of magnesium, but numerous experiments showed that the first

¹ Ber. d. chem. Ges. 22, 186.² This Journal 9, 14.

coating at *A* entirely protected the glass, so that subsequent portions of the metal were deposited without being contaminated with the silicide. Experiment also showed that the iron tube served to support the walls of the glass tube, as the latter would otherwise collapse when heated to the fusing point of magnesium. The tube at *B* was maintained at a bright red heat for about an hour, the gas was then turned down and the apparatus cooled very slowly. By taking proper precautions the cracking of the tube was prevented during the cooling process, thereby maintaining a vacuum in the apparatus until the end of the distillation. The portion of the metal remaining in *B* and that which had collected at *D* were rejected. The portion collected at *A* was three times redistilled; the magnesium which collected at *A* during the fourth distillation was employed for the atomic weight determination. It was deposited as a thin crystalline bar of pure white metal, which readily separated from the coating of magnesium silicide on the glass. In a few instances beautiful crystals of the metal were formed; these will be considered later in this paper. The magnesium deposited in the fourth distillation was carefully analysed, special pains being used in the tests for silicon, carbon, calcium and iron, but we were unable to detect any impurity whatever. It was also spectroscopically examined, but the spectrum showed no lines of impurities, the characteristic green lines of magnesium being the only ones visible. We analysed the magnesium ribbon used in the distillation and found small quantities of silicon, iron and carbon.

II. *Preparation of Pure Dilute Nitric Acid.*

Pure strong nitric acid was prepared by the method already described in this Journal.¹ In order that the magnesium might dissolve slowly, the nitric acid was diluted with an equal volume of water. The water was purified by distilling it first from acid permanganate of potassium, then from alkaline permanganate, and finally in the platinum apparatus which was used in preparing the nitric acid. The dilute acid was preserved in a platinum dish under a bell-jar, and a platinum spoon was used for transferring it as it was needed.

¹ 10, 314.

III. The Method of Procedure.

The conversion of the magnesium into its oxide was effected in porcelain crucibles, the arrangement of the crucibles being the same as that described in the article on the atomic weight of zinc. A piece of magnesium weighing about 300 milligrams was carefully broken off, and any clinging portions of dust removed by filing. A powerful lens was used in examining the metal, and it was not handled except by means of clean forceps. Having balanced a pair of crucibles with their appropriate tares, the difference in weight was noted. The piece of magnesium was then weighed into one of them and treated with dilute nitric acid. When the metal had disappeared, the excess of acid and water was evaporated, and the nitrate of magnesium partially decomposed by heating in a sand-bath. Finally the crucibles were placed in a muffle furnace and kept at a white heat for about two hours. After weighing, the oxide was again heated in the muffle, and as a rule one ignition was sufficient to insure constant weight. In some of the determinations, however, two ignitions were necessary. The tares were treated with dilute nitric acid, and heated in every instance like the crucibles in which the determinations were made. The magnesium oxide was tested for oxides of nitrogen by the method described by Griess.¹ The magnesium oxide was dissolved in dilute sulphuric acid, and two cubic centimeters each of sulphanilic acid and naphthylamine hydrochlorate were added. Not a trace of the pink color appeared. In another sample of the oxide, which was not ignited to constant weight, the iodide of starch reaction for testing for nitrous acid failed to give a blue color, while the sulphanilic acid test showed a distinct pink color.

IV. The Weighing.

The balance used was made by Becker Bros.; its capacity was one hundred grams, and it was sensitive to $\frac{1}{10}$ milligram with its full load. The balance case was inclosed in a tight-fitting wooden box, furnished with appropriate doors, through which the weights and crucibles could be transferred. All observations were made with these doors closed. A gas lamp and mirror were so arranged that the ivory scale of the balance could be illuminated through a small aperture in the box; the excursions of the pointer were

¹ Ber. d. chem. Gesell. 12, 426.

noted through a similar aperture situated just above the first. The methods of weighing by vibrations and of double weighing—that is, upon both pans—were employed throughout. The sensibility of the balance, with the load furnished by the crucibles, was determined at least once during each series of observations. Each weighing was made as rapidly as possible, allowing due time for noting observations accurately, as it is believed that an undue amount of time spent in weighing only increases the error due to changes in temperature and atmospheric conditions. Only the smaller platinum weights were used, since the magnesium oxide obtained in one experiment never weighed more than seven hundred milligrams. All weighings were made at night after the laboratory and streets in the vicinity had become quiet.

V. The Results.

The following table shows the result of ten successive experiments:

	Wt. of Mg.	Wt. of MgO.	At. wt. Mg (O = 16).	At. wt. Mg (O = 15.95). ¹
1	.33009	.54766	24.278	24.202
2	.34512	.57252	24.283	24.207
3	.26058	.43221	24.292	24.216
4	.28600	.47432	24.299	24.223
5	.30917	.51273	24.301	24.225
6	.27636	.45853	24.271	24.195
7	.36457	.60475	24.286	24.210
8	.32411	.53746	24.304	24.228
9	.32108	.53263	24.284	24.208
10	.28323	.46988	24.279	24.203
		Mean	24.287	24.211
		Highest	24.304	24.228
		Lowest	24.271	24.195
		Difference	.033	.033

If we calculate the atomic weight from the sums of the quantities of magnesium taken and oxide obtained as recommended by Meyer and Seubert,² we have:

Wt. of Mg.	Wt. of MgO.	At. wt. Mg (O = 16).	At. wt. Mg (O = 15.95).
3.10031	5.14269	24.287	24.211

¹ Value found by Keiser, this Journal 10, 249.

² Die Atomgewichte der Elemente, p. 13.

VI. Crystals of Magnesium.

Of the crystal form of magnesium very little is definitely known. The element is usually regarded as holohedral, hexagonal, and isomorphous with zinc and beryllium. The production of very perfect crystals during the distillation of our magnesium seemed of sufficient interest to warrant their study and description. Dr. G. H. Williams of the Johns Hopkins University undertook this work and kindly sent us his results for publication. The first account of magnesium crystals was given by Dumas¹ in 1880, who obtained them while experimenting with the gases absorbed by magnesium during distillation. Des Cloizeaux² measured these crystals and described them as hexagonal prisms with the unit pyramid and terminated by the basal plane. He obtained the axial ratio $a:c = 1:1.6391$.

The crystals which we obtained were about one millimeter in diameter, having very perfect planes which furnished, in most instances, sharp and distinct reflections on the goniometer. No planes appeared except OP, P and ∞P . The following table shows the angles measured on four different crystals with a large Fuess goniometer. In each crystal one or more zones of 180° were observed; when more than one zone was measured the mean result is stated and the number of zones upon which this average is based is given in parenthesis.

Crystal.	OP : P.	P : ∞P .	∞P : P'.	P' : OP'
I	$61^\circ 47' (2)$	$28^\circ 12' (2)$	$28^\circ 17'$	$61^\circ 50'$
II	$61^\circ 44'$	$28^\circ 15'$	$28^\circ 00'$	...
III	$61^\circ 55'$	$28^\circ 5'$	$28^\circ 3'$	$61^\circ 57'$
IV	$61^\circ 57' (3)$	$28^\circ 5' (3)$	$28^\circ 7' (3)$	$61^\circ 52' (3)$

The average of the twelve measurements of the angle OP : P is $61^\circ 52' 30''$; whose supplement is $118^\circ 7' 30''$. If we use this value for the axial ratio we have $a:c = 1:1.6202$, which is almost identical with the value obtained by Des Cloizeaux. It appears from these figures that magnesium is more closely related to beryllium, in its crystal form, than to zinc, as will be seen in the following statement:

Beryllium, $a:c = 1:1.5802$ Brögger.

Zinc, $a:c = 1:1.35642$ Williams and Burton (Am. Ch. Jour. **11**, 219).

Magnesium, $a:c = 1:1.6202$ Wilson.

¹ Comptes rendus **90**, 1027.

² Ibid. **90**, 1101.

Experiments were made to test the cohesive properties and slipping planes of the magnesium, but no results were obtained like those described in the investigation of zinc crystals.

It is with pleasure that we acknowledge our indebtedness to Professor Morley and Professor Mabery, who placed their laboratories at our disposal during this investigation. With such adequate facilities we were enabled to work much more rapidly and satisfactorily than we otherwise could have done.

CLEVELAND, O., February, 1890.

A MODIFICATION OF THE METHOD OF COMBUSTION WITH LEAD CHROMATE.

BY RUDOLF DE ROODE.

A modified method of combustion with lead chromate, which I have used with good results, is as follows: A mixture of about 4 parts by weight of finely divided lead chromate and 1 part by weight of red lead, after thorough washing, is sucked into a compact mass on a funnel with a pump. While still moist, the mass is divided with a spatula into lumps about the size of a pea. These lumps are heated to redness in small portions in a porcelain crucible. While hot they are of a dark brown or black color, but on cooling in the air the color changes to a bright red. The lumps are broken up in a mortar to about the size of grains of wheat. The larger grains are separated by a sieve from the smaller particles, which are pulverised and used for mixing with the substance to be analysed.

Into a combustion tube of a suitable length for the furnace is placed an asbestos plug (*A*), in front of which a piece of reduced copper gauze is to be put. From recent experiments it has been shown that the presence of this copper is necessary, whether the substance to be analysed contains nitrogen or not. The tube is then filled to about two-thirds of its length with the coarse grains of the preparation, which are held in place by a second asbestos plug (*B*). Behind this plug is introduced the substance to be analysed, mixed with some of the finely powdered preparation. The mixing is best accomplished as follows:

The tube is held in a vertical position with the front end down. On top of the asbestos plug (*B*) a layer of the finely powdered preparation about two inches thick is introduced by means of a small copper funnel. The weighed substance, on a small watch-glass, is then introduced through the funnel, and the glass, funnel, and walls of the tube rinsed with small portions of the finely powdered preparation until a second layer of about two inches in thickness has been added (to *E*). The substance (which is now at *C*) is mixed intimately with the fine powder (from *B* to *E*), either by means of a clean copper wire, or better, by closing the end of the tube and shaking and turning it about in the tube. The remainder of the tube (to *F*) is then filled with the coarsely granular preparation. A channel is made for the free passage of the gases along the entire length of the tube by striking it longitudinally on a flat surface. The tube is placed in the furnace, connected in front with the calcium chloride tube, potash bulbs, etc., and behind with an apparatus furnishing pure dry air. The clamp (at *G*) is closed tight and the tube heated in front (nearly up to *B*) to a bright red heat. The gas-jets are then turned on from behind (at *F*), and the combustion conducted as usual. When the combustion is completed the apparatus is connected with an aspirator, which is set in operation and pure dry air admitted by opening gradually the clamp (*G*), by which clamp the current of air may be regulated. The tube is kept hot, especially at the portion (*BE*) where the substance was contained, for about 10 or 15 minutes while the current of air is being drawn through. The tube is then allowed to cool slowly while about a liter of air is drawn through. The weighed bulbs and tubes are then disconnected, the tube closed tightly in front, and left in connection with the dry air behind until cool. If not broken, the tube may be used over and over without disturbing the portion between *A* and *B*. The stopper is taken out behind and the coarse grains (from *F* to *E*) removed. The portion (from *E* to *B*) which contained the substance is scraped out and discarded. The tube is then filled



as before for another combustion, a fresh piece of reduced copper gauze being put in front, if necessary.

This granulated mixture of lead chromate and oxide does not fuse at a red heat, thus rendering it preferable to pure, fused lead chromate. In the granulated form it presents a larger surface of action than powdered lead chromate, and thus possesses all of the advantages of copper oxide.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

A SELF-REGULATING GAS-GENERATOR ON A NEW PRINCIPLE.

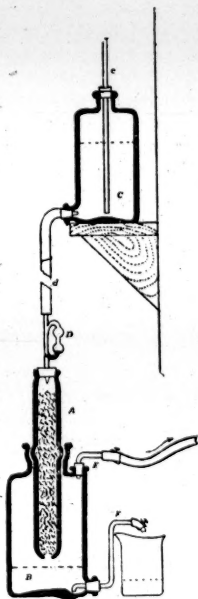
BY H. W. HILLYER.

The accompanying diagram illustrates a form of gas-generator devised by the writer especially to supply hydrogen sulphide for this laboratory. But as the apparatus seems to have several points of advantage over those now in use, in cases where large quantities of gas are to be generated; where a considerable pressure is required; and where the apparatus does not often need to be moved, it may be found useful in other places if made known by this notice.

The apparatus consists of two principal parts, the acid reservoir (*C*) and the generator (*AB*). The acid reservoir is a common aspirating bottle of a gallon or more capacity, provided with a stopper and glass tube (*c*) to regulate the liquid pressure, on the principle of the Mariotte bottle. A piece of stout rubber tubing (*d*) connects it with a bulb tube (*D*) drawn out at its lower end to an opening of about one-sixteenth of an inch in diameter and passing through the rubber stopper in the cylinder (*A*). The generator consists of the glass cylinder (*A*) and the outer glass vessel (*B*) which are ground or cemented together gas-tight. The cylinder (*A*), about two and a half inches in diameter and twenty inches in length, serves to hold the ferrous sulphide, zinc or marble over which the acid trickles or rather is forced by the gas generated. The vessel (*B*), about nine inches in diameter and eighteen in height, serves two purposes, first as a reservoir for waste acid, secondly, as a reservoir in which is stored gas generated and not immediately needed.

The acid flows from (C) through (d) and (D) into (A). The gas generated, finding no outlet at the top of the cylinder, forces the acid over the contents of the cylinder into (B) and escapes through (E). When a less rapid evolution of gas is required, its flow through (E) is checked, the pressure inside the generator soon becomes great enough to balance the column of acid, which stops flowing so rapidly, and the generation of gas is diminished or ceases entirely if (E) is fully closed. A too sudden and excessive accumulation of pressure, which might force the acid out of (Dd) back into (C) or drive out the stoppers, is prevented by having the vessel (B) of large capacity. If (E) is closed suddenly, even when the apparatus has been working quite rapidly and a considerable quantity of acid is still acting on the solid reagent, the capacious vessel gives room for much gas before a high pressure is reached, so that the flow of acid is stopped gradually and without excessive strain on the apparatus. To guard against any possible forcing of the acid back into (C), enough mercury is put in the bulb tube to fill the lower bend. It offers but little resistance to the flow of the acid, since it spreads out in the bulb, but when it is forced back into the narrow vertical part of the tube it adds materially to the opposition to be overcome in driving the acid from the tube back into the acid reservoir.

The height at which the acid reservoir is placed depends on the pressure desired. For ordinary work in the laboratory where the maximum pressure is that required to charge with hydrogen sulphide two ordinary five-pint bottles in series, three feet of vertical distance from the lower end of tube (c) to the lower end of tube (D) is about right. This is enough to balance the back pressure of the mercury and to insure rapidity of action against the maximum pressure mentioned. The acid reservoir is filled by



removing its upper stopper and tube, preferably after closing the pinch-cock on (*d*). The acid used in making hydrogen sulphide is crude muriatic acid diluted with two parts of water. The waste solution drips into (*B*) so nearly neutral that it is black with precipitating ferrous sulphide and so dilute that there is no danger of any salt crystallising out. It is removed by opening the pinch-cock on the tube (*E*), when the pressure in the generator forces it out into the beaker or other vessel placed to receive it. The cylinder (*A*) is filled by removing its rubber stopper after closing the pinch-cock on (*d*). Its contents should not be finely broken, that is, it is best to reject all which will pass through a sixteen-mesh sieve. Perhaps a good average size is that of peas. The material is supported by a piece of coarse iron wire gauze on which the exhausted acid has little, if any, action.

The chemical building of the University of Wisconsin has a special room in the basement, in which hydrogen sulphide is generated and operations may be performed requiring large use of that gas. From this room lead pipes extend to fume closets in each of the two principal laboratories, where they terminate in a row of gas-cocks with small openings. With the above described apparatus connected with this pipe system a student has only to attach his glass tube to one of the gas-cocks and open it a sufficient amount to let the hydrogen sulphide flow at the desired rate. On completing his precipitation or saturation he has only to shut off the gas and detach. In connection with this large pipe system there is one peculiar difficulty. When the waste solution is drawn off at (*E*) the pressure in the generator may be so much lowered that the water in an ordinary wash-bottle would be forced into the generator by the pressure in the pipes. To obviate this two wash-bottles are used, so placed that the longer tubes of each are connected together. Of the shorter tubes one is connected with the generator and one with the pipe system. The bottle nearest the pipes is the real wash-bottle and ordinarily contains the wash-water, but this is emptied into the other bottle without harm done whenever the pressure in the generator is less than that in the pipes.

The apparatus is made and can be obtained of Mr. Emil Greiner of New York.

That it may work perfectly it must not leak, and consequently must be well made to resist the considerable pressure to which its joints are subjected.

ON THE CHLORINE COMPOUNDS OF TOLANE.

BY ARNOLD EILOART.

The Two Tolane-dichlorides.

For the stereo-chemical formulae for these two compounds,



α , plane-symmetrical,
of higher melting point.



β , center-symmetrical,
of lower melting point.

experimental proofs have already been offered by Blank.¹ These proofs depend on the relative quantities of the two chlorides which result from the reduction of the tetrachloride with zinc dust and alcohol. The present investigation was carried out in the laboratory of Professor Wislicenus, at his suggestion, for the purpose of further testing these formulae, by determining (1) the relative stability of the two chlorides, (2) the possibility of the production of one or both of the chlorides by the chlorination of tolane. For the theory of Wislicenus² not only declares that there must be between these isomers a considerable difference in stability, but enables us to foretell that only that modification which may prove to be the less stable can be formed directly and without any intermediate product by the simple addition of chlorine to tolane. In the first place, therefore, with a view to comparing the relative stability of the chlorides, quantitative investigations were made (1) as to their behavior at high temperatures, (2) as to their resistance to the reducing action of zinc dust.

Preparation of the Tolane-dichlorides.

These were made from tolane-tetrachloride, which was prepared at first by the method indicated by Hanhart³ and worked out by Blank, by treating benzotrichloride, diluted with benzene, with reduced copper. The product of the action, after concentration, consisted chiefly of a black tarry mass, from which the crystals it contained could be separated only with great difficulty. To obtain a better result I now tried the experiment without the benzene,

¹ Ann. Chem. (Liebig) **248**, 17.

² Joh. Wislicenus: Ueber die räumliche Anordnung der Atome in organ. Molec. Leipzig, 1887.

³ Ber. d. chem. Ges. **15**, 898.

heating the copper with the benzotrichloride alone, and varying the time, the temperature, and the proportion of the substances. These experiments enabled me to confirm the observation of Hanhart, who noticed a very violent reaction between the copper and the benzotrichloride, accompanied by evolution of fumes and by rise of temperature. Onufrowicz,¹ on the other hand, remarks that in his experiments the reaction went quite quietly. The phenomena observed by Hanhart repeated themselves in my experiments, although not till the temperature reached 105° C. That the temperature of the water-bath was not, as in Hanhart's case, sufficient was due probably to a difference in the reducing power of the copper employed. Still the yield remained very unsatisfactory, and finally, to use up the tarry residues, they were distilled under diminished pressure, and in this way the tolane-dichlorides were obtained at once, although in no great quantity.

The tetrachloride was now prepared from benzil. It proved best to add at once the excess of phosphorus pentachloride necessary for the formation of the tolane-tetrachloride, and not first to prepare the dichlorbenzil. Even in this way the latter was formed in considerable quantity, as was proved by the melting point and by the percentage of chlorine in the by-product.

0.2807 gram substance gave 0.3088 gram AgCl.

	Theory for $C_6H_5.CO.CCl_2.C_6H_5.$	Found.
Cl	26.8	27.17

When allowed to crystallise slowly from petroleum ether, the dichlorbenzil formed beautiful transparent plates, with oblique angles, and easily to be obtained 2 cm. long.

From 88 grams benzil 44 grams of nearly pure tetrachloride were at once obtained. For recrystallising it petroleum ether (b. p. 110°) is to be recommended. This, when hot, dissolves the tetrachloride much more freely than does alcohol, and when cold dissolves much less than does benzene.

To prepare the tolane-dichlorides from the tetrachloride and to separate them from one another, the method detailed by Blank was followed. The separated dichlorides were then recrystallised from alcohol until the melting points were constant. The plane-symmetrical chloride fused then at 139.5°, which agrees with Hanhart's observation, while Zinin² and Limpricht and Schwan-

¹ Ber. d. chem. Ges. 17, 833.

² Ibid. 4, 289.

ert¹ found 153°, and Liebermann and Homeyer,² Onufrowicz (l. c.) and Blank found 143°. The center-symmetrical chloride fused at 58°; Hanhart gives 60°, other authors 63°.

Behavior of the two Dichlorides when heated.

Zinin³ distilled these substances and only mentions that they come over undecomposed. According to Limpricht and Schwannert (l. c.), each chloride is, on distillation, partially converted into the other. Blank⁴ states that, whichever of the two chlorides be distilled, the composition of the distillate is the same; it contains, namely, seven parts of the center-symmetrical to three of the plane-symmetrical. And Blank says:

"This is to be accounted for by the application of Wislicenus' explanation of the conversion by heat of unsaturated compounds into compounds geometrically isomeric. As soon as the heat loosens the bonds of the atoms in the molecule, one chloride can turn into the other. Then, of course, the molecules of the more favored form, *i. e.* those having the axis- (= center-) symmetrical form, will be found in greater number than those of the plane-symmetrical configuration, and the relative proportion of the two forms will alter with the temperature, but for any particular temperature will be constant."

The question was to subject to an exact test these dicta of the theory.

For heating the substances a vapor-oven of copper was used. With this the temperature in the inner air-space could be kept constant for hours within half a degree. The vapors of boiling cumene (b. p. 153°), aniline (b. p. 183°) and benzoic ether (b. p. 213°) were used in succession. The experiments were conducted throughout in the same way. Into a small, thin-walled tube, closed at one end, were weighed exactly 2 grams of the one chloride, and into a similar tube 2 grams of the other; the tubes were then put each into a thick-walled one, and the latter sealed. The sealed tubes were then laid side by side in the oven. This had already been heated to constant temperature. Opening it lowered this temperature, and the time of heating was reckoned from the moment when the original temperature was restored. After cooling, the contents of each tube were brought by means

¹ Ber. d. chem. Ges. 4, 379.

² Jahresbericht, 1871, 438.

³ Ibid. 12, 1971.

⁴ Ann. Chem. 248, 18.

of 20 grams absolute alcohol into an Erlenmeyer flask, and dissolved with the aid of heat. Any crystals which separated out on cooling were collected on a weighed filter, and washed with about 10 grams alcohol. The filtrate was always evaporated to apparent dryness in a weighed Erlenmeyer flask, placed aslant on the water-bath. The residue in the flask was then left to stand *in vacuo* over sulphuric acid, together with the crystals on the weighed filter. If the flask be left on the water-bath after the alcohol odor has disappeared, some of the solid contents volatilise. Accordingly the residue, after being weighed, was warmed only till it melted, in order to expose a fresh surface for the evaporation of all traces of alcohol. The flask was then left again in the desiccator from which the air had been exhausted. The melting and drying in the desiccator were repeated till the weight was constant.

On the filter remained now only the slightly soluble α - or plane-symmetrical dichloride, the weight of which is shown in Table I, Col. 6; the residue from the filtrate consisted mostly of the easily soluble β - or center-symmetrical chloride, but contained also some α -chloride, the amount of which was yet to be determined. To this end the weight of the alcoholic filtrate was always taken (Table I, Col. 4), and by subtracting from this the weight of the dried residue, the weight of the alcohol to be considered was arrived at. But the solubility of the plane-symmetrical chloride in pure alcohol is quite different from its solubility in alcohol containing center-symmetrical chloride. The results given in Table I are therefore only preliminary.

TABLE I.

1.	2.	3.	4.	5.	6.	7.
Experiment.	Taken.	Time.	Temp.	Alcoholic filtrate.	Residue from filtrate.	On filter. Total Col. 5+ Col. 6.
I. {	Plane, 2 gr.	2 hours.	{ 143° — 177 }	25 gr.	0.1444	1.8498
	Center, 2			20	dissolved everything.	1.9942
II. {	Plane, 2	2	177	21.43	0.1937	1.7989
	Center, 2			20	dissolved everything.	1.9926
III. {	Plane, 2	3	177-204	29.20	0.7494	1.2419
	Center, 2			33.49	1.7533	not determined.
III ^a . {	Plane, 2	3	204	27.16	0.7954	1.2041
	Center, 2			28.07	0.7405	1.2391
IV. {	Plane, 2	10	206	34.5	1.3316	0.6430
	Center, 2			29.0	1.5102	0.4729
IV ^a . {	Plane, 2	10	204½	36.13	1.3664	0.6204
	Center, 2			33.14	1.5400	0.4372
V. {	Plane, 2	slowly distilled.	265-350 +	30.07	1.4531	0.5330
	Center, 2			28.22	1.4741	0.5061
V ^a . {	Plane, 2	distilled very fast.		30.47	1.3593	0.6353
	Center, 2			29.79	1.4445	0.5369

The table shows that the sum of the weights of the products obtained is in nearly every case rather less than the weight of substance taken. Nevertheless no appreciable decomposition had taken place, for even at the highest temperatures the product after heating was but slightly colored, and on opening the tube neither pressure nor escape of gas was to be noticed. Besides, the weight of the tube and contents remained unaltered on opening.

There was, however, a source of loss detected. After the residue from the alcoholic filtrate had attained constant weight, alcohol was added till the solution had again the weight of the original filtrate. The weight of the residue left, on again evaporating, was always a few milligrams less than before, and this number of milligrams, representing the chloride which had volatilised with the alcohol, is therefore to be added to the weight originally found. Thus in the last experiment (V^a, Table I), starting with the plane-symmetrical chloride, the sum of the weights of the dissolved and of the undissolved portions obtained was 1.9946 gram. To the dried dissolved portion alcohol was added till the weight was that of the original filtrate, 30.47 grams. After evaporating the alcohol the weight of the residue was 0.0053 gram less than at first: $1.9946 + 0.0053 = 1.9999$. Starting with the center-symmetrical chloride, the corresponding figures were $1.9814 + 0.0104 = 1.9918$. So that the unavoidable loss is very small.

And the loss by volatilisation can affect only the center-symmetrical chloride, for the amount of the plane-symmetrical chloride contained in the filtrate is arrived at quite independently. And since the determinations of the plane-symmetrical chloride proved more exact of execution than those of the other, the amount of change was calculated only from the former, while the weight of the dissolved portion served as a control.

On the separate experiments given in the table the following remarks may be made:

Experiment I.—As the α -chloride did not fuse when heated in cumene-vapor, the heating of both chlorides was continued with aniline-vapor.

Experiment III.—After heating an hour with aniline-vapor (since Experiment II showed so little change at this temperature), the heating was continued in the vapor of benzoic ether. From the solution of the β -chloride, the less soluble product appeared this time not in one of the known forms of the α -chloride crystals,

in oblique-angled plates, or in nitre-like columns, but in needles, such as the center-symmetrical chloride forms, but more pointed and harder than these. On this account the determination of the undissolved portion was in this experiment given up, and the substance was subjected to further examination. After washing with alcohol the slightly soluble crystals fused, without any recrystallisation, at 138° —almost at the melting point of the plane-symmetrical chloride. Under the microscope not a single crystal of prismatic form could be seen among the needles. The small quantity which was left after washing was now used for a chlorine determination.

0.0733 gram substance heated to 220° four hours in a sealed tube with AgNO_3 and HNO_3 gave 0.086 gram AgCl .

	Theory for $\text{C}_{14}\text{H}_{10}\text{Cl}_2$.	Found.
Cl	28.51	29.02

In Experiment IV exactly similar needles were found in larger quantities; their solubility was nearly the same as that of the plane-symmetrical chloride.

	Alcohol.	Dissolved.	Dissolved by 100 grs. alc.	Temp.
Needles	26.361 grams	0.149 gram	0.565	19°
Plane-chloride { (1)	47.401 "	0.2763 "	0.583	
(plates) { (2)	40.087 "	0.2332 "	0.582	

In fact these needles change on recrystallisation and even on simply standing with alcohol, into the ordinary oblique-angled plates. They are accordingly nothing but plane-symmetrical chloride. Later this chloride, when obtained from solutions which contained much of its isomer, appeared always in this form, and sometimes the needles were 2 cm. long.

Experiment V.—Of each chloride 3 grams were distilled successively, the same air-bath and distilling flask being used for each. The temperature was kept as low as possible; with both chlorides it varied between 265° and over 350° . At first the chlorides came over white, later yellowish. From 3 grams of the center-symmetrical I obtained 2.66 grams, from 3 grams plane-symmetrical 2.81 grams of distillate. Of each distillate 2 grams were used for analysis, as shown in the table.

Experiment V.—2.6 grams center-symmetrical chloride distilled from the air-bath as quickly as possible, and without taking the temperature, gave 2.47 grams; and 2.6 grams plane-sym-

metrical chloride gave 2.43 grams of distillate. In both cases the distillate was white. Again 2 grams of each distillate were used.

Now before we can review the outcome of these experiments as a whole, each result must be subjected to the correction for the amount of plane-symmetrical chloride dissolved by the alcohol.

Solubility of the Tolane-dichlorides in Alcohol.

Determinations were made as follows:

	Alcohol, grams.	Dissolved, gram.	Dissolved by 100 grs. alcohol.	Temp.
Plane-symm. chloride	48.371	0.3437	0.710	24.4°
Center-symm. chloride	4.492	0.4721	10.51	
Plane- and center-symm. } chlorides together	3.827	0.4182	10.93	25.6°

If we add to the amount of plane-symmetrical chloride dissolved at 24.4°, the amount of center-symmetrical dissolved at the same temperature, we find the sum ($0.71 + 10.51 = 11.22$) to be .29 per cent. higher than the amount of the mixed chlorides which is dissolved even at the temperature 25.6°.

Had this diminution of solubility been divided between the two chlorides in the proportion of their solubilities, only a small part of it would have fallen on the plane-symmetrical chloride. But that this was the chloride whose solubility was chiefly affected was proved as follows. To a saturated solution of center-symmetrical chloride was added a little less of the other than the alcohol alone would have dissolved. By warming complete solution was effected. On cooling, although the balance showed that there had been practically no loss of alcohol, crystals separated out. Their solubility (unwashed) was but little greater than that of the plane-symmetrical chloride.

	Alcohol, grams.	Dissolved, gram.	Dissolved by 100 grs. alcohol.	Temp.
The crystals	1.278	0.012	0.939	27°
Plane-symm. chloride	28.792	0.2085	0.724	

The converse experiment was made by dissolving in alcohol saturated with the plane-symmetrical chloride and then warmed, rather less of the other chloride than the alcohol when cold would have dissolved. After cooling, alcohol was added to make up the slight loss of weight due to evaporation. The solubility of the crystals which separated out was determined.

Alcohol.	Dissolved.	Dissolved by 100 grams alcohol.	Temp.
1.491 gram	0.0123 gram	0.825	23.3°

This quantity of alcohol would dissolve 0.0106 gram of pure plane-symmetrical chloride or only 1.7 mgm. less.

The remarkable manner in which the solubility of the less soluble was lowered by the presence of the more soluble chloride led me to estimate the proportion of the plane-symmetrical chloride so thrown out of solution. It was found that from a saturated solution of plane-symmetrical chloride more than 56 per cent. of it was precipitated by the addition of center-symmetrical chloride.

Next, in order to eliminate from my results the effects of this varying solubility, mixtures of the two chlorides in known proportion were made, and these were treated exactly as the unknown mixtures had been treated in order to separate their components. The sum of the two chlorides was always two grams, and the proportions were so chosen that the weight of the chloride left on the filter in each experiment should be nearly the same as in one of the previous experiments. In these, as in the previous separations, the same temperature, 19° C., was closely adhered to; and here, too, 20 grams alcohol were used for dissolving and about 10 grams for washing. The filtrate was weighed in each experiment, and from this weight was deducted the weight of the residue left on evaporation. In Table II the weight of the plane-symmetrical chloride taken is given under *a*, and under *b* that of the residue on the filter. In every case *a* was mixed with (2 - *a*) grams of the other chloride. The weight of the alcohol in the filtrate is called *B* and the product $\frac{a-b}{B} \cdot 100$, or the amount of the plane-symmetrical chloride dissolved by 100 grams alcohol is called *S*.

TABLE II.

Experiment.	<i>a</i> .	<i>b</i> .	<i>a-b</i> .	<i>B</i> .	<i>S</i> .	<i>S</i> mean.
I. { 1	0.3333	0.264	0.0693	28.07	0.2469	} 0.246
2	0.3333	0.270	0.0633	25.85	0.2449	
II. { 1	0.6666	0.5481	0.1185	31.10	0.381	} 0.374
2	0.6666	0.5680	0.0986	26.90	0.367	
III. { 1	1.3333	1.204	0.1293	29.69	0.4355	} 0.440
2	1.3333	1.218	0.1153	25.91	0.4450	

With the values of *a* as abscissae, and those of *S* as ordinates, these results are represented in the curve below. Besides passing

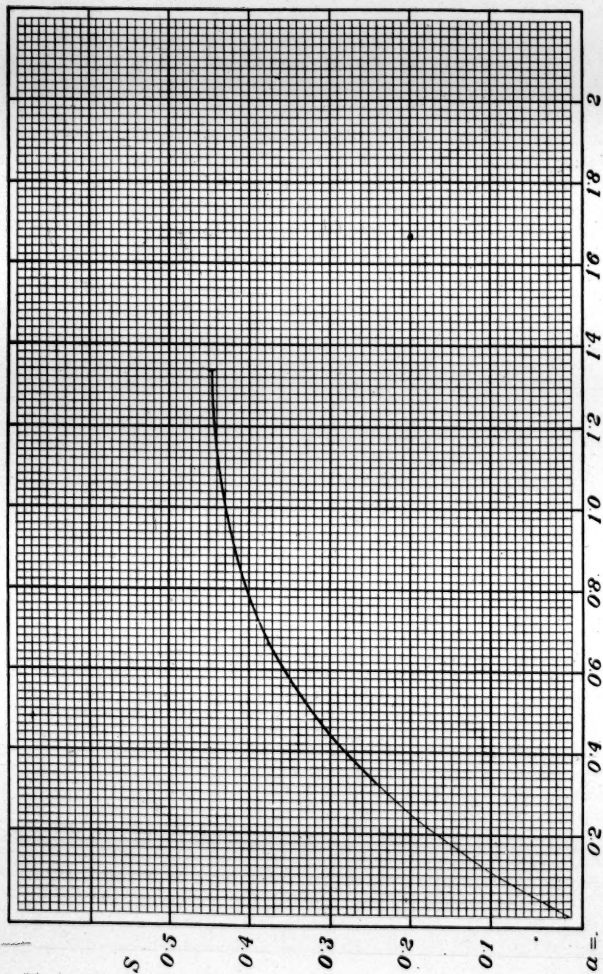
through the points indicated by Table II, the curve must of course pass through the origin of the system.

Table III shows the results of Table I corrected for the solubilities indicated by the curve. But the proportions of the known mixtures were so chosen that even without applying the curve the directly determined coefficients of solubility would suffice for a close approximation, except in the case of Experiment "IV" (Center)," where the difference would be 0.013 gram. In the table, Col. 1 gives the plane-symmetrical chloride weighed on the filter (= Col. 6, Table I), *S* is the coefficient of solubility indicated by the curve for each mixture, *B* the weight of alcohol in the filtrate, and therefore $\frac{S \times B}{100}$ is the weight of the plane-symmetrical chloride dissolved. For the reasons given, the amount of chloride changed is reckoned from the weight of plane-symmetrical chloride obtained. This final result of the series of experiments is given in Col. 8 as "Conversion per cent.," *i. e.* the percentage of altered substance.

TABLE III.

Experiment.	1	2	3	4	5	6	7	8
	On filter.	<i>S</i> .	<i>B</i> .	$\frac{S \times B}{100}$	Plane chloride (Col. 1 + Col. 4).	Time.	Temp.	Con- version per cent.
II. {								
Plane,	1.7989	0.582	21.24	0.1236	1.9225	2 h.	177°	3.88
Center,			20 dissolved	everything.				
III. {								
Plane,	1.2419	.440	28.45	.1252	1.3671	3	177°-204°	31.65
Center,								
III ^a . {								
Plane,	1.2041	.440	26.46	.1164	1.3205	3	204°	33.98
Center,	0.2391	.230	27.33	.0628	0.3019			15.09
IV. {								
Plane,	0.6430	.393	33.17	.1303	0.7733	10	206°	61.34
Center,	0.4729	.353	27.49	.0970	0.570			28.5
IV ^a . {								
Plane,	0.6204	.388	34.76	.1348	0.7552	10	204½°	62.24
Center,	0.4372	.333	31.60	.1052	0.5424			27.12
V. {								
Plane,	0.5330	.368	28.62	.1053	0.6383	slowly	265-350+	68.09
Center,	0.5061	.359	26.75	.0961	0.6022	distilled.		30.11
V ^a . {								
Plane,	0.6353	.388	29.11	.1129	0.7482	distilled very fast.		62.59
Center,	0.5369	.368	28.35	.1043	0.6412			32.06

From the last three columns it is at once evident how with both chlorides the conversion of one into the other increases with the temperature and with the time, and how this conversion attaining a maximum leaves only 31.91 per cent. of the plane-symmetrical chloride unchanged (Experiment V), while of the center-symmetrical chloride only 32.06 per cent. are changed (Experiment V^a);



Curve showing the solubility, S , in grams per 100 grams alcohol, of the plane-symmetrical tolane-dichloride when a grams of it are mixed with 2 — a grams of center-symmetrical chloride.

the conversion being thus, within 0.15 per cent., complementary for the two chlorides, so that the final products from both have the same composition.

The whole series of experiments places it beyond all doubt that, as the theory of Wislicenus declares, the center-symmetrical chloride is far more stable than its isomer.

That the two chlorides when heated in the same way did not yield distillates of the same composition is to be accounted for by the fact that they do not distill at the same temperature. For according to Hanhart (l. c.), the plane-symmetrical chloride boils at 260° – 280° , and the other at 310° – 313° . They must therefore be distilled at different temperatures if we wish to expose them for the same time to the heat. Accordingly we must compare not the two experiments "V Plane" and "V Center," but "V Plane" and "V^a Center."

By calculating for the different pairs of results the ratio of the altered chlorides, which is the same as the ratio of the velocities with which they change into one another, we obtain in every case almost the same figures.

From Table III, Column 8, we have:

	III ^a .	IV.	IV ^a .
Altered Plane,	33.98	61.34	62.24
Altered Center,	15.09	28.5	27.12
Ratio $\frac{\text{Plane}}{\text{Center}}$,	2.25	2.15	2.29
Mean,	2.23		

But for the reasons just mentioned, we must compare "V Plane" with "V^a Center," and "V^a Plane" with "V Center."

	V Plane, V ^a Center.	V ^a Plane, V Center.
Altered Plane,	68.09	62.59
Altered Center,	32.06	30.11
Ratio $\frac{\text{Plane}}{\text{Center}}$,	2.12	2.07

Indeed, from the three experiments conducted at 204° we can calculate within one per cent. the maximum attainable conversion, *i. e.* the composition of the product when the *equilibrium mobile* is established. For the mean value 2.23 calculated above for the

ratio $\frac{\text{Plane}}{\text{Center}}$ at 204° corresponds to

69.04 per cent. Plane and 30.96 per cent. Center,
the maximum found being

68.09 per ct. (V Plane) and 32.06 per ct. (V^a Center).

Difference 0.95

1.1

And this in spite of the fact that in the latter experiments a change of state had taken place, and that as the distillations were completed in two or three minutes, the velocities of conversion were several hundred times greater in them than in the experiments at 204° ; still the ratio of the velocities remained almost constant.

But in this case where the alteration of the coefficient of equilibrium κ (i. e. the ratio of the velocities of conversion) due to change of temperature is zero, the heat of conversion, ς , is also zero, according to the equation given by Van't Hoff,¹

$$\frac{d(\kappa)}{dT} = \frac{\varsigma}{0.02 T^2}.$$

Within the limits of error of these experiments, then, there is in the change of the tolane-dichlorides into one another neither development nor absorption of heat, and the heat of combustion must be for both chlorides nearly the same.

Further, we can to some extent compare the effects of an increase of temperature on the chlorine atoms in the molecules of the two chlorides. If we call the distance between the two chlorine atoms in the one molecule x , and in the other y , and let these be the values for a certain definite temperature, while $x + b$ and $y + b'$ are the values for another definite temperature; then, since the ratio of the velocities of conversion remains the same at different temperatures, and since this ratio would vary if the ratio of the distances between the chlorine atoms in the two molecules varied (unless, indeed, the effect of such variation should be eliminated by compensating variations in the distances of other atoms), we have

$$\frac{x}{y} = \frac{x+b}{y+b'} \text{ and } \frac{x}{y} = \frac{b}{b'}$$

And if $x \pm y$, which according to the theory of geometric isomerism would hold in the case of the chlorine atoms, then $b \pm b'$. Either, therefore, the oscillations of the chlorine atoms in the

¹ Cf. Ostwald, Lehrbuch der allgemeinen Chemie 2, 737.

molecule of the one chloride, caused by rise of temperature, are unequal to those of the chlorine atoms of the other, caused by the same rise of temperature, or these oscillations make no appreciable difference in the distances between the atoms, i. e. b and b' vanish in comparison with x and y .

Bearing of the Experiments described on the Results obtained by Blank.

In view of the remarkably variable solubility of the plane-symmetrical chloride proved above, it is evident that those of Blank's results,¹ in which this solubility comes into consideration, require a correction. Blank added ethyl alcohol (in some experiments amyl alcohol) to 20 grams tolane-tetrachloride and reduced with zinc dust. He determined the quantities of the dichlorides so obtained and comments thus on the results:

"If we consider the numbers obtained for the plane-symmetrical chloride, we find that according to the theory they are too high. Since, as already explained, tolane-tetrachloride can have for every two molecules of the more favored configuration [of the space-formula] at most only one molecule of the less favored, and since 20 grams tolane-tetrachloride correspond to 15.56 grams dichloride, there should be formed at most $\frac{15.56}{3} = 5.19$ grams of plane-symmetrical chloride; but at 80° and at 130° this limit is exceeded."

Now in these experiments about 200 cc. or 160 grams alcohol were used for dissolving the chlorides, and the plane-symmetrical chloride contained in this was calculated as if its solubility had been the same as in alcohol containing no center-symmetrical chloride. At the temperature of these experiments, 160 grams of pure alcohol dissolved, according to Blank, 1.08 gram or 0.675 per cent. plane-symmetrical chloride. The temperature is not mentioned; but still my experiments render possible an approximate correction. For, at the temperature at which I found the solubility of the plane-symmetrical chloride *per se* to be 0.582 per cent., the solubility of the plane-symmetrical chloride, when mixed with twice its weight of center-symmetrical chloride, was only 0.374 per cent. At the temperature then at which Blank found the solubility of the plane-symmetrical chloride *per se* to be 0.675

¹ Loc. cit. p. 27.

per cent. ($=0.582 + 0.093$), the solubility of the plane-symmetrical chloride, when he had it mixed with twice its weight of center-symmetrical chloride, could not have been *more* than $0.374 + 0.093 = 0.467$ per cent.

It may be objected that my coefficients of solubility, although available for the correction of my own experiments, must be too low, since part of the alcohol was used only for washing, and was not left 24 hours in contact with the substance, as was the case in Blank's work. But this does not cause low results. The alcohol used for washing, being free from center-symmetrical chloride, dissolves proportionally more of the plane-symmetrical chloride than does alcohol left 24 hours in contact with the mixed chlorides. Thus two mixtures of $1\frac{1}{2}$ gram center- with $\frac{1}{2}$ gram plane-symmetrical chloride gave, after separation with alcohol in the usual way, residues of the latter chloride which were thoroughly freed from center-symmetrical chloride, and on further washing yielded filtrates consisting of:

I. 10.075 grams alcohol and 0.0478 gram chloride.

II. 10.042 grams alcohol and 0.044 gram chloride; or 100 grams alcohol dissolve, I. 0.474, II. 0.438; whereas in Table II the solubility of the plane-symmetrical chloride in the presence of twice its weight of center-symmetrical chloride is only 0.374 per cent.

Accordingly, we may take as stated 0.467 per cent. as more than the maximum that could have been dissolved in Blank's experiments. The degree of concentration was almost exactly the same in his experiments as in mine. In the latter there were, before the washing with alcohol, which we have already taken into consideration, in 20 grams alcohol $1\frac{1}{2}$ gram center-symmetrical chloride, or 6.66 per cent., and half that quantity of plane-symmetrical chloride; in the former there were in 160 grams alcohol about 10.37 grams ($\frac{15.56}{3} \times 2$) or 6.48 per cent. center-symmetrical chloride, and half that quantity of plane-symmetrical chloride. Accordingly the quantity of plane-symmetrical chloride dissolved from such a mixture by 160 grams alcohol could not be more than $160 \times 0.467 = 0.747$ gram.

Let us apply this figure to Blank's results.

In his paper these stand thus:

Taken 20 grams tolane-tetrachloride.

I. At 80° C.	(1). Plane-sym. chloride separated, .	4.2	grams.
	Dissolved in 200 cc., ...	1.08	
	Total, ...	5.28	
	(2). Plane-sym. chloride separated, .	4.31	
	Dissolved in 200 cc., ...	1.08	
	Total, ...	5.39	

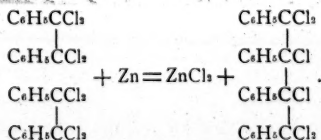
Corrected, they stand thus :

I. At 80° C.	(1). Plane-sym. chloride separated, .	4.2	grams.
	Dissolved in 200 cc. alcoholic		
	solution of center-sym., . .	0.75	
	Total, ...	4.95	
	(2). Plane-sym. chloride separated, .	4.31	
	Dissolved in 200 cc. alcoholic		
	solution of center-sym., . .	0.75	
	Total, ...	5.06	

Theoretical maximum, 5.19 grams.

Hence the theoretical limit is at 80° C. certainly not exceeded. How far a similar correction would alter the somewhat higher results obtained with amyl alcohol is matter for further experiment. If they should be lowered to the same extent, they too would, within the limits of error of the experiments, coincide with the theoretical number.

Such a simple explanation of the discrepancy between the results and the theory is the more satisfactory, because the explanation given by Blank cannot be accepted as final. This explanation depends on the formation, in the reduction of the tolane-tetrachloride, of an intermediate product, "ditolane-hexachloride." Its formation is represented, according to Blank, by the equation



Now since, as Blank found, one molecule of the plane-symmetrical chloride can unite with one molecule of toluene-tetrachloride to form the hexachloride, it would not be surprising if, in spite of the careful manner in which the whole series of Blank's experiments was carried out, a little tetrachloride, converted in this way into hexachloride, had been weighed with the plane-symmetrical chloride, especially since the solubility of the hexachloride is, as will be shown later, almost the same as that of the plane-symmetrical chloride.

Blank's explanation is, however, quite different. The hexachloride, as he shows, yields, on further reduction, more plane- than center-symmetrical chloride, and to this he attributes the excess of plane-symmetrical chloride obtained from the tetrachloride.

"The formation," says Blank, "of the hexachloride from the tetrachloride does not take place quantitatively. If we allow just so much zinc dust to act on the latter as suffices for its decomposition, we get from 20 grams tetrachloride about 9.3 grams hexachloride, together with 7.4 grams of the axial-symmetrical chloride, *i. e.* to one molecule of hexachloride about two of dichloride. In this reaction no plane-symmetrical chloride whatever is formed. Only through the further action of zinc dust do we get the latter, and 10 grams hexachloride gave (I) 6 grams, (II) 5.9 grams plane-symmetrical chloride" (l. c. p. 29).

According to this the 9.3 grams hexachloride obtainable from 20 grams tetrachloride would yield 5.53 grams plane-symmetrical chloride. So that when the formation of the hexachloride is favored to the utmost (cf. Blank, l. c. p. 28), even then the theoretical limit, 5.19 grams, for the plane-symmetrical chloride is exceeded by only 0.34 gram. This hardly explains the fact that in an experiment (l. c. p. 27) conducted without adherence to the conditions favorable to the formation of hexachloride, the theoretical limit for the plane-symmetrical chloride was still further exceeded, viz. at 130° by 0.46 gram.

But Blank supports his explanation for the excessive yields of plane-symmetrical chloride by theoretical reasons also. The space-formula of the hexachloride proves, he says, that this must yield on reduction more plane- than center-symmetrical chloride. That the hexachloride is a homogeneous body, that it has in fact only one space-formula, is, however, not yet proved. Such a view

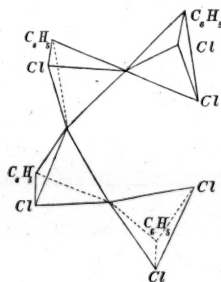
is contradicted by the result of a determination of its molecular weight conducted by Blank according to Raoult's method. With regard to this determination Blank says: "This result would indicate, since there can be no tolane-trichloride, that the hexachloride is not a homogeneous compound, but a mixture of tolane-di- and tetra-chloride crystallising together. But several of the chemical facts which have been mentioned are opposed to this idea, more particularly the formation of this body out of *both* the dichlorides by the action of chlorine or on treatment with the tetrachloride. Since these facts carry more weight than the result of Raoult's method, which has not yet been proved applicable to every class of substances,¹ the substance investigated must be accounted homogeneous and described as ditolane-hexachloride" (l. c. p. 33). In the experiment with chlorine, which was passed into the fused chlorides, the temperature is not given. But the process is a complicated one; "there are formed together with oily liquids certain quantities of ditolane-hexachloride," and the possibility of the conversion of the chlorides one into the other is not excluded.

On treatment with the tetrachloride, the formation of the hexachloride from the center-symmetrical chloride did not result, as was the case with the plane-symmetrical chloride, through merely heating the alcoholic solution of the two bodies, but the substances had to be heated for half an hour at 180° , a temperature, according to Blank, "at which the dichlorides do not begin to change one into the other." But, according to my experiments, the temperature at which the two chlorides begin to change one into the other is 177° or lower, and at 180° it is quite possible that even in half an hour in presence of the tetrachloride, if this takes up every trace of plane-symmetrical chloride as fast as it is formed, removing it from the sphere of action, considerable quantities of the latter might be formed, and thus cause the formation of hexachloride.

But however the solid hexachloride may be constituted, it follows, from reasons presently to be given, that the hexachloride dissolved in alcohol, as well as (according to the lowering of the freezing point) that dissolved in benzene, behaves like a mixture of plane-symmetrical chloride and tetrachloride.

¹ But we are indebted to Blank himself for the successful application of Raoult's method to the tolane-dichlorides, which surely belong to the same class of substances with the hexachloride.

But suppose the hexachloride dissolved in alcohol to possess the space-formula given by Blank. The explanation based on this is still unsound. Giving four configurations of the formula as possible, Blank describes three as yielding plane- and center-symmetrical molecules in equal numbers, while one yields plane-symmetrical molecules only. But the configuration which gives plane-symmetrical chloride only,



is just the least favored of all; for here, in every case, negative components (chlorine atoms) stand opposite negative, and positive components (phenyl groups) opposite positive in corresponding positions. Now, even if the temperature should be high enough to cause this configuration to occur as frequently as each of the three more favored ones, we should still have from the four configurations only five molecules of plane- to three molecules of center-symmetrical chloride, whereas the proportion actually found was more than two to one.

I here give the quantities obtained by Blank, together with the figures calculated according to this application of his theory.

Reduced: 10 grams ditolane-hexachloride.

	Found.		Theory for 5 plane to 3 center.
	I.	II.	
Plane-sym. chloride, . . .	6.0	5.9	5.45
Center-sym. chloride, . . .	2.7	2.9	3.27

I now offer a more simple explanation of the facts.

Not only the ratio of one to two just referred to, but also the circumstance that "the formation of the hexachloride from the

tetrachloride does not take place quantitatively"; that "from 20 grams tetrachloride we get about 9.3 grams hexachloride, together with 7.4 grams of the axial-symmetrical chloride, *i. e.* to one molecule of hexachloride about two of dichloride"; moreover, that "in this reaction no plane-chloride whatever is formed"; all these facts and figures are explained by the hypothesis rejected by Blank, that the hexachloride is a mixture of tetrachloride and dichloride (plane-symmetrical, to wit) crystallising out together; so that in the reduction of the tetrachloride with zinc, the hexachloride results only from the union of the tetrachloride with plane-symmetrical chloride, and therefore only so many molecules of hexachloride can be formed as there were molecules of plane-symmetrical chloride formed beforehand; whence follows that the quantity of plane-symmetrical chloride formed by dechlorination of the tetrachloride cannot be increased, but only diminished by the formation of hexachloride; and therefore it was that with a maximum yield of hexachloride "no plane-symmetrical chloride whatever was formed." This view explains at once why in the reduction of the tetrachloride there were formed two molecules of axial- (center-) symmetrical chloride to every one of hexachloride: simply because for every two molecules of center-symmetrical chloride there is formed one of plane-symmetrical, and this uniting with one molecule of tetrachloride gives one molecule of hexachloride.

Further, if the dissolved hexachloride represents a molecule of tetrachloride and a molecule of plane-symmetrical chloride, how would it behave when treated with zinc dust and alcohol, so as to form the dichloride from it? Exactly as the experiments show it does behave.

For simplicity let us consider three "molecules" of hexachloride as consisting of three molecules of plane-symmetrical chloride and three molecules of tetrachloride. The three former would remain unchanged. The three latter would yield as usual one molecule of plane- and two molecules of center-symmetrical chloride. Thus the three molecules of hexachloride would yield altogether four molecules of plane- to two of center-symmetrical chloride.

I here give the quantities obtained by Blank, together with the figures calculated on this theory.

Reduced: 10 grams hexachloride.

	Found.		Theory for 2 plane to 1 center.	
	I.	II.	Mean.	
Plane-sym. chloride,	6.0	5.9	5.95	5.83
Center-sym. chloride,	2.7	2.9	2.8	2.92
	8.7	8.8	8.75	8.75

This is the strongest proof that ditolane-hexachloride does not exist in alcoholic solution as a homogeneous substance. In these figures, too, we again have evidence that the quantity of plane-symmetrical chloride has been over-estimated.

Action of Zinc-dust on the Tolane-dichlorides dissolved in Alcohol.

Zinin¹ observed that in this action tolane is formed. Liebermann and Homeyer,² by continuing the action for several days, brought the amount of chlorine which remained united with the tolane down to 6 per cent. Nowhere is anything said as to a quicker reduction of one chloride than of the other. But the theory of Wislicenus enables us to affirm that such a difference exists. For the chlorine atoms in the center-symmetrical chloride, held fast by their proximity to the phenyl groups, will not be so readily detached as will those in the plane-symmetrical chloride, which are in corresponding positions in the molecule. And in fact the difference is great, as the following experiments prove.

These experiments were conducted throughout in the same way. A solution of 1 gram center-symmetrical chloride in 150 grams alcohol was heated to boiling, the heat was removed and 2 grams of well purified zinc dust were immediately added. The solution was then kept boiling on the water-bath for a definite time, an inverted condenser being used; then the solution was quickly cooled and filtered at once from the zinc dust. The latter was washed with cold alcohol and dissolved in sulphuric acid. From this solution the chlorine (from any zinc oxychloride which might have been formed) was precipitated by silver nitrate. The chlorine was also precipitated in the alcoholic filtrate, and finally the two precipitates were weighed together. One gram of plane-symmetrical chloride was treated in exactly the same way.

Since in the first experiment no reduction had taken place, more zinc dust was prepared, and washed this time only once with hydrochloric acid, and then as before with water, alcohol and ether.

The results are here tabulated.

¹ Jahresbericht, 1871, 438.

² Ber. d. chem. Ges. 12, 1971.

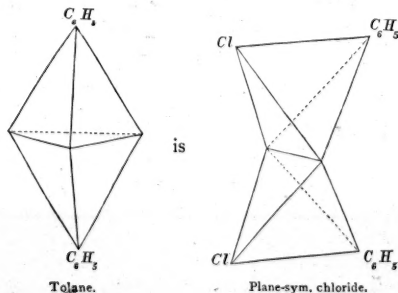
Reduction of the Tolane-dichlorides with Zinc-dust and Alcohol.

	Chloride.	Zinc I.	Time.	AgCl found.	=Chlorine.	Cl from Chloride.	Chloride Reduced.	per cent.
		2 grs.		0.0052	0.0013	...	...	...
I. { Plane,	1 gr.	2 "	} 5 min.	0.0088	0.0022	...	...	...
	1 "	2 "		0.0106	0.0026	...	...	...
	Center,	1 "						
		Zinc II.		0.0206				
		2 grs.		0.0144	0.0043	...	...	...
II. { Plane,	1 gr.	2 "	} 3 hrs.	0.0714	0.0176	0.0133	0.047	4.7
	1 "	2 "		0.0160	0.0039	...	...	...
	Center,	1 "						
III. { Plane,	1 gr.	2 grs.	} 10 hrs.	0.3918	0.0968	0.0925	0.325	32.5
	Center (a),	1 " 2 "		0.0770	0.0190	...	...	...
	Center (b),	1 " 2 "		0.0704	0.0174	0.0139	0.049	4.9

Thus in three hours no noticeable reduction of the center-symmetrical chloride had taken place, and in ten hours the reduction was hardly more than that effected in three hours in the case of the plane-symmetrical chloride. In both the action goes on faster after some time than at first.

The Products of the Chlorination of Tolane.

According to Liebermann and Homeyer (l. c.), on passing chlorine into a solution of tolane in chloroform, the tolane-dichloride fusing at 143° was produced. The theoretical explanation of this result is given in the treatise of Wislicenus already mentioned. For the only configuration which can result from the simple addition of two atoms of chlorine to



since whichever carbon-bond is broken the chlorine atoms can take only corresponding positions.

The experiments on this process are incomplete, but the results so far obtained thoroughly corroborate the theory. I repeated the experiment of Liebermann and Homeyer, using, instead of chloroform, pure carbon bisulphide (as little as possible) to dissolve the tolane. In a preliminary qualitative experiment the solution, cooled with ice and kept in the dark, was saturated with chlorine and left over night in an atmosphere of the gas. Then the carbon bisulphide was driven off by a stream of dry air. There remained a sticky, partly solid mass. This was dissolved in ten times its weight of hot alcohol. On cooling, the solution gave crystals amounting to about half the weight of the chlorinated product. After recrystallisation from alcohol the fusing point of the crystals was constant at 148° . They were short, thick, white prisms, of rhombic or quadratic appearance, and contained the same amount of chlorine as Blank's ditolane-hexachloride (fusing point 150°).

0.3043 gram substance heated 4 hours with HNO_3 and AgNO_3 to 220° , gave 0.4625 gram AgCl .

	Theory for $\text{C}_{28}\text{H}_{20}\text{Cl}_6$.	Found.
Cl	37.35	37.60

This ditolane-hexachloride seems to be identical with a body obtained by Limpricht and Schwanert¹ by heating tolane with phosphorus pentachloride to 170° . Their compound also crystallised in white prisms fusing at 150° , and "a chlorine determination indicated the composition $\text{C}_{11}\text{H}_5\text{Cl}_3$ " (L. & S.). The amount of chlorine found is not given; the theoretical amount for $\text{C}_{11}\text{H}_5\text{Cl}_3$ is 37.56 per cent.

The solubility of the hexachloride in alcohol was almost the same as that of the plane-symmetrical chloride.

Temp.	Alcohol.	Dissolved.	Dissolved by 100 grs. Alcohol.	Mean.
24°	24.47	0.1834	0.7493	0.744 per cent.
	23.96	0.1771	0.7393	

At 24.5° the solubility of the plane-symmetrical chloride was 0.7104 per cent. So that if the latter had been formed it would not have been separated from the hexachloride by the recrystallisation, and must have made the percentage of chlorine come out

¹ Ber. d. chem. Gesell. 4, 379.

too low. The dichloride had therefore not been formed (as such), for in the mother-liquors also nothing but hexachloride could be found.

The experiment was now made quantitatively. 5 grams tolane treated exactly as before yielded, after air had been passed through till the weight was constant, 8.9592 grams chlorinated product, or only 0.041 gram less than if the whole had been converted into tetrachloride. On recrystallising I obtained 4.7225 grams hexachloride. This corresponds to 2.968 grams tolane. The remaining 2.032 grams tolane had given, then, 4.2367 (8.9592—4.7225) grams of the chlorinated product. So that this part of the product contained 52 per cent. of chlorine. It consisted of a red sticky mass in which crystals gradually formed. As no solvent effected a satisfactory separation of the crystals, the chlorine was determined in the mixture just as it was. An exact result was, of course, not to be expected, especially since in the evaporation of the alcoholic filtrates from the hexachloride a volatilisation of 0.233 gram of the substance had taken place. Still the chlorine determination confirmed the result of the above calculation—namely, that besides the hexachloride there had been formed a substance which contained more chlorine than even the tetrachloride.

0.1372 substance gave 0.2675 gram AgCl, corresponding to 47.43 per cent. of chlorine; while the tetrachloride contains only 44.3 per cent.

These experiments prove that in the chlorination of tolane about 60 per cent. of it is converted into "ditolane-hexachloride." There are also formed oily products containing much chlorine.

Now, through the application of my former results to those of Blank we have gained an insight into the constitution of the hexachloride. This view we may in turn apply to the result of the last experiments. For since the hexachloride consists of tetrachloride and plane-symmetrical chloride, the molecules of both these substances must have been formed in the formation of the hexachloride from tolane. And thus the theory is once more confirmed by the proof of the production of the plane-symmetrical chloride.

THE ELECTROMOTIVE FORCE OF METALLIC SALTS.

BY CLARENCE L. SPEYERS.

Owing to the close connection between chemical action and manifestation of electricity, the study of electrical action promises, if it does not solve, at least great assistance towards the solution of the problem, "What is chemical action?" How brilliantly Ostwald's investigations on electrical conductivity of solutions, aided by the dissociation hypothesis of Arrhenius and others, have illuminated chemical phenomena! The darkness surrounding solution,¹ diffusion, electromotive force between solutions of different concentration, thermo-neutrality, etc., has been dissipated. True, the light *may* be false and vanish, but it is the first ever shed on questions hitherto so obscure. If, then, the study of one phase of electrical conduction has taught so much, it is not unreasonable to expect something from an investigation of another side, namely, the separation of electricity or production of an electromotive force.

Ordinary self-continued chemical changes are accompanied by a loss of energy (appearing in the form of heat), and it is natural to suppose that with proper arrangements all this heat can be converted into a corresponding quantity of electricity. In fact, Sir W. Thomson suggested this view. Experience, however, has shown that such a statement does not express the truth; a correction is required which, by some, is supposed to be caused by secondary reactions; by others, with Helmholtz at the head, to be due to the existence of two states of energy, the free and the bound. Applying thermo-dynamics to reversible cells, Helmholtz obtains an expression representing the difference between the chemical (as measured in heat) and the electrical energies consumed and developed respectively in the cell. Experience tells that now the case is correctly stated from a mathematical point of view, but the chemical explanation still remains to be discovered. How this will be achieved is of course at present uncertain, but will it not probably be through the study of the simplest

¹ The writer does not admit that any distinctions are to be made between physical and chemical action other than those of degree and convenience. Of course, mechanical action is excluded.

cases in which an electromotive force is produced? At any rate, it was with this hope that the following investigation was commenced, the plan being to measure the electromotive force of solutions of metallic salts and its variation on systematic dilution. The present paper deals with hydrogen and zinc salts of Cl , NO_3 , $\text{C}_2\text{H}_3\text{O}_2$, and SO_4 .

Instead of zinc, an amalgam of this metal was chosen for two reasons: first, the surface presented to the liquid might be considered as homogeneous; secondly, a tarnishing of the brilliant surface would readily reveal any secondary reaction due to oxidation or hydration. With very few exceptions, whenever the electromotive force had an abnormal value, an examination of the amalgam showed an alteration of the surface, evidenced either by a dull film or loss of mobility. The apparent exceptions were probably due to such a thin film that an alteration of surface could not be perceived but nevertheless existed. The anomalous values were sometimes too high, sometimes too low. Observations were suspended when tarnishing was unmistakably shown. Experiments by Lindeck¹ and others showed that less than 1 per cent. of zinc imparted to mercury an electromotive force equal to that of zinc, justifying the substitution of an amalgam containing 1 per cent. of zinc. Hydrogen amalgam not being available, a zinc amalgam was also used with the acids. The negative electrode was composed of pure mercury, so as to neutralise, as far as possible, any chance alteration of electromotive force due to a change of surface tension.

The mercury was purified by causing it to trickle through a solution of mercurous nitrate, comparative experiments showing that this method was as effective and far more convenient than heating with concentrated sulphuric acid.

All liquids contained one gram equivalent in a liter of water, and, whenever possible, measurements were commenced with solutions of this strength. Zinc chloride and sulphate solutions were prepared by dissolving proper quantities in water, but to obtain solutions of zinc nitrate and acetate, other methods were necessary, owing to the formation of basic salts. The former was successfully made by carefully neutralising normal nitric acid with pure zinc oxide, using tropæolin as an indicator. The latter, by double decomposition between barium acetate and zinc sulphate,

¹ Wied. Ann. 35, 311.

titrating the resulting filtrate with potassium ferrocyanide and diluting with the proper quantity of water. In this way $\frac{1}{2}$ equivalent¹ solution of zinc acetate was easily obtained free from any basic salt.

For measuring the electromotive force a capillary electrometer and compensation cells were used. The method has been so fully described by Ostwald² that anything more would be superfluous. To evaluate the electromotive force between the binding posts of the resistance-box as well as that of the compensation battery, two Clark cells were constructed according to Lord Rayleigh's directions.³ As no difference could be detected when the two cells were opposed, although the electrometer was sensitive to less than 0.0001 V, their electromotive force was considered equal to

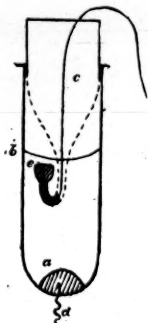


FIG. 1.

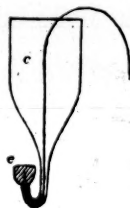


FIG. 2.

$1.435 [1 - 0.00077 (t - 15)]$ V. At the close of the present series of experiments a slight inequality (0.001 V) was observable, which, however, could readily be accounted for by a large fluctuation in the temperature of the room during a few cold winter nights, and the Clark cells not having an equal temperature at the time of measurement. Every two weeks the electromotive of the compensation cells was determined, and every day that between the two binding-posts of the resistance-box, the latter being measured by the aid of a compensation cell.

¹ One gram equivalent in two liters of water.

² Zeitschrift f. physikal. Chem. 1, 403.

³ Elementary Pract. Physics, Stewart and Gee, 2, 481.

The cell containing the liquid to be experimented upon is outlined in the two figures. *b* is a portion of a thick test-tube drawn out and a platinum wire fused through the bottom *d*. This tube, with a capacity of about 15 cc., contains the solution and amalgam *a*. Another piece of test-tube is drawn out, a platinum wire inserted and the glass fused around it, at the same time bending the drawn-out portion upward so as to form a cup *e*, in which a globule of mercury can be placed. The platinum wire makes a metallic connection. The piece *c* must be drawn out in such a manner that when the cup is made its orifice is below the surface of the solution contained in *b*. By grinding *c* into *b* a glass stopper is formed, enabling the liquid to be thoroughly mixed after each dilution. Fig. 1 shows *b* and *c* in position; Fig. 2, *c* alone. Four such cells were constructed, enabling duplicate measurements to be made with two solutions at the same time.

The manner of operation was this: Two pipettefuls of the solution were introduced, and then about 0.25 cc. of the carefully cleansed amalgam, the stopper inserted, and the tube gently rocked to and fro, care being taken to fill the cup of the stopper with liquid. The cup was then filled with mercury, which displaced the liquid (the stopper being removed for this purpose), and proper connection made with the electrometer. When the electromotive force became constant, the value was recorded, the mercury in the cup tossed out, the liquid gently shaken, a fresh globule of mercury introduced, and another measurement made. If they did not coincide, the process was repeated until a satisfactory agreement was obtained.¹ Half the liquid being removed, an equal volume of distilled water was added and the above process repeated until the amalgam tarnished. Constant values were often reached in a few minutes with concentrated solutions, but as dilution proceeded a longer interval was required, which in one case (zinc nitrate and sulphuric acid) extended over 60 hours.² Usually, however, 24, but sometimes 12 hours were sufficient for a series. Now and then, the electromotive force would rise and then fall continuously. Under such circumstances the highest value was recorded, justification being found in the fact that no constant value could be obtained by waiting, for the electromotive force decreased continuously throughout a long

¹ In a few cases, noted in the tables, satisfactory results could not be obtained.

² For the completed series.

period of observation. This procedure, however, was only adopted when the highest value of the duplicate was sensibly the same. Such abnormal behavior was observed only with dilute solutions and concentrated acids: caused in the former case, probably, by a slight alteration of the surface of the amalgam; in the latter, by hydrogen evolved from the platinum wire, when the latter was exposed to the strong acid while in contact with the amalgam.

The temperature at which the experiments were made was that of the room, about 20° C.

In the following tables the column headed v contains the number of liters of water in which a gram equivalent of the salt has been dissolved, that headed E. F. the corresponding electromotive force in volts (10⁸ C. G. S.), and that headed Δ the difference between successive values of E. F. Any deviation from the mean exceeding one per cent. is noted in the tables. The observations have all been duplicated and sometimes quadruplicated.

v	$\frac{1}{2}\text{HCl}^1$			$\frac{1}{2}\text{HNO}_3$			$\frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$			$\frac{1}{2}\text{H}_2\text{SO}_4$			$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HNO}_3$		
	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ	
1	1.1477			1.4335			1.4244			1.4680			1.1540		
2	1.1010			1.4370			1.4417	0.0173		1.4688			1.1053		
4	1.1701			1.4417			1.4415	0.0002		1.4633	0.0055		1.1820		
8	1.1903			1.4458			1.4545	0.0130		1.4643	0.0010		1.1969		
16	1.2064	0.0161		1.4560	0.0102		1.4530	0.0015		1.4649	0.0006		1.2154	0.0185	
32	1.2262	0.0198		1.4475	0.0085		1.4549	0.0019		1.4644	0.0005		1.2271	0.0117	
64	1.2390	0.0128		1.4475	0.0120		1.4573	0.0024		1.4673	0.0029		1.2466	0.0195	
128	1.2561	0.0172		1.4595	0.0008		1.4573	0.0003		1.4673	0.0035		1.2466	0.0112	
256	1.2682	0.0120		1.4603	0.0101		1.4570	0.0030		1.4708	0.0029		1.2578	0.0180	
512	1.2800	0.0118		1.4704	0.0003		1.4540	0.0030		1.4737	0.0014		1.2758	0.0113	
1024	1.2898	0.0098		1.4707	0.0003					1.4751			1.2871	0.0101	
															
		0.0142			0.0041			0.0037			0.0008			0.0143	
v	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$			$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{H}_2\text{SO}_4$			$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$			$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4$			$\frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$		
	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ	
1	1.1402			1.1618			1.4373			1.4485			1.4410		
2	1.1630			1.1765			1.4414			1.4400			1.4457		
4	1.1780			1.1912			1.4455			1.4507			1.4405		
8	1.1933			1.2059			1.4406			1.4518			1.4533		
16	1.2120	0.0137		1.2172	0.0113		1.4489	0.0007		1.4501	0.0017		1.4519	0.0036	
32	1.2269	0.0149		1.2270	0.0098		1.4531	0.0042		1.4544	0.0043		1.4519	0.0040	
64	1.2375	0.0126		1.2389	0.0119		1.4607	0.0136		1.4560	0.0076		1.4670	0.0061	
128	1.2565	0.0170		1.2566	0.0177		1.4691	0.0024		1.4603	0.0017		1.4665	0.0005	
256	1.2678	0.0113		1.2767	0.0201		1.4790	0.0029		1.4637	0.0034		1.4672	0.0007	
512	1.2868	0.0188		1.2941	0.0174		1.4743	0.0023		1.4584	0.0053		1.4764	0.0092	
															
		0.0147			0.0147			0.0041			0.0011			0.0038	

¹ The numbers printed in italics are calculated by subtracting once, twice, etc., the mean increment from the first observation. On account of the rapid evolution of hydrogen a stronger acid than $\frac{1}{2}$ th equiv. could not be used.

² Observations varied in some cases about one per cent. from the mean.

v	$\frac{1}{2}\text{ZnCl}_2$			$\frac{1}{2}\text{Zn(NO}_3)_2$			$\frac{1}{2}\text{Zn(Ac)}_2$			$\frac{1}{2}\text{ZnSO}_4$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{Zn(NO}_3)_2$		
	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ	
1	1.0865	0.0195		1.3219	0.0307		1.2508			1.2750	0.0209		1.0978	0.0279	
2	1.1060	0.0208		1.3526	0.0187		1.2691	0.0100		1.2959	0.0190		1.1257	0.0210	
4	1.1288	0.0282		1.3743	0.0152		1.2800	0.0087		1.3149	0.0208		1.1467	0.0197	
8	1.1570	0.0261		1.3865	0.0193		1.2887	0.0084		1.3357	0.0247		1.1664	0.0211	
16	1.1771	0.0178		1.4058	0.0045		1.2971			1.3604	0.0233		1.1875	0.0192	
32	1.1949			1.4103	0.0160					1.3837			1.2067	0.0210	
64				1.4203									1.2277	0.0192	
128													1.2510	0.0210	
256		0.0217			0.0174		0.0093				0.0217			0.0219	
$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{Zn(Ac)}_2$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{ZnSO}_4$			$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{Zn(Ac)}_2$			$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{ZnSO}_4$			$\frac{1}{2}\text{Zn(Ac)}_2 + \frac{1}{2}\text{ZnSO}_4$			
v	E. F.	Δ	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		
1	1.1043		1.0956	0.0208		1.2512	0.0034		1.2751	0.0282		1.2703			
2	1.1250	0.0208	1.1164	0.0215		1.2689	0.0034		1.3033	0.0261		1.2837	0.0254		
4	1.1458	0.0207	1.1379	0.0262		1.2651	0.0558		1.3294	0.0240		1.3151	0.0210		
8	1.1665	0.0201	1.1641	0.0212		1.3212	0.0189		1.3534	0.0158		1.3301	0.0128		
16	1.1866	0.0202	1.1853	0.0204		1.3401	0.0241		1.3692	0.0248		1.3489	0.0084		
32	1.2068	0.0202	1.2057	0.0204		1.3642	0.0069		1.3949	0.0248		1.3573	0.0084		
64	1.2284	0.0216							1.4051	0.0111					
128									1.4252	0.0201					
256									1.4407	0.0155					
$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HCl}$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HNO}_3$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HAc}$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$						
v	E. F.	Δ	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		
1	1.0889	0.0269	1.0988	0.0270		1.1088	0.0249		1.1070	0.0291		1.1070	0.0291		
2	1.1158	0.0207	1.1258	0.0208		1.1267	0.0220		1.1361	0.0207		1.1361	0.0207		
4	1.1365	0.0210	1.1466	0.0150		1.1487	0.0207		1.1568	0.0207		1.1568	0.0207		
8	1.1573	0.0211	1.1675	0.0192		1.1694	0.0258		1.1775	0.0204		1.1775	0.0204		
16	1.1786	0.0228	1.1817	0.0202		1.1952	0.0230		1.1979	0.0204		1.1979	0.0204		
32	1.2014	0.0200	1.2019	0.0221		1.2182	0.0221		1.2191	0.0212		1.2191	0.0212		
64	1.2214	0.0200	1.2240	0.0250		1.2403	0.0221		1.2393	0.0211		1.2393	0.0211		
128	1.2436	0.0200	1.2490	0.0208		1.2606	0.0241		1.2604	0.0192		1.2604	0.0192		
256	1.2636		1.2698	0.0195		1.2847	0.0200		1.2766	0.0173		1.2766	0.0173		
512			1.2893	0.0195		1.3047	0.0239		1.2969			1.2969			
1024		0.0219		0.0212		1.3278				0.0211			0.0211		
$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{HCl}$			$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{HNO}_3$			$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{HAc}$			$\frac{1}{2}\text{Zn(NO}_3)_2 + \frac{1}{2}\text{H}_2\text{SO}_4$						
v	E. F.	Δ	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		
1	1.0955	0.0301	1.3581	0.0301		1.3154	0.0300		1.3106	0.0460		1.3106	0.0460		
2	1.1256	0.0207	1.3888	0.0161		1.3454	0.0223		1.3696	0.0256		1.3696	0.0256		
4	1.1463	0.0197	1.4043	0.0158		1.3677	0.0171		1.3912	0.0226		1.3912	0.0226		
8	1.1660	0.0212	1.4201	0.0135		1.3848	0.0139		1.4178	0.0040		1.4178	0.0040		
16	1.1872	0.0195	1.4336	0.0206		1.3977	0.0171		1.4218	0.0155		1.4218	0.0155		
32	1.2067	0.0206	1.4362	0.0080		1.4148	0.0153		1.4373	0.0029		1.4373	0.0029		
64	1.2273	0.0214	1.4442	0.0063		1.4301	0.0004		1.4400	0.0060		1.4400	0.0060		
128	1.2487	0.0209	1.4505	0.0019		1.4395	0.0009		1.4460	0.0208		1.4460	0.0208		
256	1.2706	0.0198	1.4524			1.4596			1.4668			1.4668			
512	1.2894														
1024		0.0216		0.0118			0.0163			0.0184			0.0184		
$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HCl}$			$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HNO}_3$			$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HAc}$			$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$						
v	E. F.	Δ	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		
1	1.1013		1.3122			1.3077			1.2987			1.2987			
2	1.1248	0.0236	1.3282	0.0199		1.3197	0.0083		1.3210	0.0157		1.3210	0.0157		
4	1.1484	0.0203	1.3481	0.0119		1.3280	0.0173		1.3267	0.0243		1.3267	0.0243		
8	1.1687	0.0214	1.3800	0.0177		1.3459	0.0187		1.3660	0.0212		1.3660	0.0212		
16	1.1901	0.0249	1.3977	0.0165		1.3646	0.0105		1.3822	0.0261		1.3822	0.0261		
32	1.2150	0.0208	1.4142	0.0160		1.3751	0.0150		1.4083	0.0221		1.4083	0.0221		
64	1.2358	0.0208	1.4302	0.0058		1.3901	0.0016		1.4304	0.0245		1.4304	0.0245		
128	1.2566	0.0212	1.4244			1.3917			1.4549			1.4549			
256	1.2778	0.0212													
512	1.3046	0.0268													
1024	1.3363	0.0317													
$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HCl}$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HNO}_3$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HAc}$			$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$						
v	E. F.	Δ	E. F.	Δ		E. F.	Δ		E. F.	Δ		E. F.	Δ		
1	1.0889	0.0269	1.0988	0.0270		1.1088	0.0249		1.1070	0.0291		1.1070	0.0291		
2	1.1158	0.0207	1.1258	0.0208		1.1267	0.0220		1.1361	0.0207		1.1361	0.0207		
4	1.1365	0.0210	1.1466	0.0150		1.1487	0.0207		1.1568	0.0207		1.1568	0.0207		
8	1.1573	0.0211	1.1675	0.0192		1.1694	0.0258		1.1775	0.0204		1.1775	0.0204		
16	1.1786	0.0228	1.1817	0.0202		1.1952	0.0230		1.1979	0.0204		1.1979	0.0204		
32	1.2014	0.0200	1.2019	0.0221		1.2182	0.0221		1.2191	0.0212		1.2191	0.0212		
64	1.2214	0.0200	1.2240	0.0250		1.2403	0.0221		1.2393	0.0211		1.2393	0.0211		
128	1.2436	0.0200	1.2490	0.0208		1.2606	0.0241		1.2604	0.0192		1.2604	0.0192		
256	1.2636		1.2698	0.0195		1.2847	0.0200		1.2766	0.0173		1.2766	0.0173		
512			1.2893	0.0195		1.3047	0.0239		1.2969			1.2969			
1024		0.0219		0.0212		1.3278				0.0211			0.0211		

¹ Observations varied in some cases about one per cent, from the mean.

² Observations varied in some cases about two per cent, from the mean.

p	$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HCl}$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HNO}_3$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HAc}$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{H}_2\text{SO}_4$	
	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ
1	1.1039		1.2964		1.5932		1.3228	
2	1.1264	0.0225	1.3177	0.0213	1.3150	0.0218	1.3521	0.0293
4	1.1466	0.0202	1.3447	0.0270	1.3386	0.0236	1.3839	0.0318
8	1.1670	0.0204	1.3678	0.0231	1.3224	0.0238	1.4154	0.0315
16	1.1882	0.0212	1.3974	0.0296	1.3809	0.0185	1.4471	0.0317
32	1.2100	0.0218	1.4128	0.0154	1.4024	0.0215	1.4663	0.0192
64	1.2342	0.0242	1.4480	0.0352	1.4250	0.0226	1.4753	0.0090
128	1.2550	0.0208	1.4570	0.0090	1.4434	0.0184	1.4774	0.0021
256	1.2750	0.0200	1.4624	0.0054				
512	1.2937	0.0187	1.4732	0.0108				
		0.0211		0.0196		0.0215		0.0221

Until more data have been accumulated, the above results cannot be most intelligently discussed, but a glance at the tables will show a few interesting facts.

1. The electromotive force always increases on dilution; the increment of nitric, acetic, and sulphuric acids is very slight, it is true, but still sufficiently marked, in the opinion of the writer, to be unmistakable. At any rate, there is no diminution, and therefore the equivalent electromotive force (electromotive force $\times$ equivalent weight, due account being taken of the quantity contained in the liquid) increases rapidly.

2. Hydrochloric acid has a much lower value than the other three acids, which form a group by themselves, with approximately equal values. It may appear strange that this acid should have an electromotive force so much inferior to that of acetic acid, but the agreement of repeated measurements indicated that they were correct.

3. The electromotive force of a mixture of equal equivalents of an acid with hydrochloric acid is not the mean of the two values, but is only slightly greater than that of hydrochloric acid. The increment also belongs to this acid. Nitric, acetic, and sulphuric acids have an electromotive force so nearly alike that no conclusion can be drawn from their mixtures.

4. Turning to the zinc salts, we find a drop in electromotive force of 33(Cl), 59(NO₃), 166(Ac), and 129(SO₄) millivolts. The first observed values, $\frac{1}{2}$ equivalent, are compared. The increment, however, has been increased. As the solutions are diluted, the fall due to substitution of zinc for hydrogen appears to approach that observed with chlorine, 33 millivolts.

5. Again, the chloride possesses the lowest electromotive force, the other three salts forming a group by themselves, with zinc

nitrate standing out prominently, the latter being caused, in the writer's opinion, by a slight defect in neutralisation, although all care was observed to avoid excess of either constituent.

6. The electromotive force of concentrated mixtures of zinc salts is not the mean of the two values, but only slightly greater than the smaller; zinc acetate and sulphate mixture possibly forming an exception.

7. Turning to mixtures of salts containing the same acid radical but different metals, we find only an approximation to the lower value, and with an increment about equal to that of the zinc salt.

8. Hitherto, chemical action has been excluded, but now consider mixtures of salts and acids having different acid radicals. As might be expected, the electromotive force is only slightly greater than that of the salt having the lower value. It must be remembered that acetic acid is very weak, so that only small quantities of acetates can be formed in the presence of equivalent quantities of the other acids.

9. The electromotive force of $\frac{1}{2}\text{ZnR} + \text{HR}'$ is equal to that of $\frac{1}{2}\text{ZnR}' + \text{HR}$. The agreement is not satisfactory, however, with zinc nitrate and sulphuric acid.

In the next paper it is purposed to describe the results of investigations upon salts of copper.

UNIVERSITY OF MISSOURI, COLUMBIA, MO., *February, 1890.*

THE USE OF ANIMAL CHARCOAL IN THE DETERMINATION OF FAT (ETHER EXTRACT) IN FEEDING STUFFS.

BY H. J. PATTERSON.

The crudeness of the product which goes under the term "ether extract" in fodder analyses is a thing that has impressed itself upon all who have to any extent been engaged in the determination of the various constituents of farm products. How to get rid of a portion, if not all, of this extraneous matter, and have nothing but fat or very closely allied products, has been an interesting question, up to this time unsolved.

To obviate this difficulty I have successfully used animal charcoal, and have obtained a product which in many cases was nearly pure vegetable oil, and in no instance could much foreign matter be detected, getting in every case a product having the general appearance and characteristics of pure fats.

The preparation of the sample and manner of treating the extract has been precisely that adopted by the Association of Official Agricultural Chemists. In filling the percolator tube there was first placed in it the animal charcoal, on top of this a plug of cotton, then the substance to be extracted, and finally another plug of cotton. The cotton serves to make a more uniform stream of ether over the substance, and keeps the latter from crawling up the sides of the percolator.

The plug between the substance and the charcoal will prevent any of the fat coming in contact with the charcoal before it is thoroughly in solution. In a few instances, especially in the case of grains, it was found that the results were a little too low if the fat came in contact with the charcoal before it was thoroughly held in solution by the ether.

In all cases one gram of the substance was used. With grains and meals one gram of charcoal was used, and with hay, fodders, and the like, two grams. The amount of charcoal can be varied at the discretion of the analyst, but the above amounts were found satisfactory. The animal charcoal was a pure article, of medium fineness, thoroughly dried, extracted with ether, and again dried and preserved for use in a well-stoppered bottle. The cotton was of good quality and clean, and had been extracted with ether previous to use.

In the following discussion the method of the Association of Official Agricultural Chemists is designated as Method I, and where charcoal has been employed as Method II.

To prove that there is no loss in passing of pure fat through charcoal, a number of fats were absorbed on cotton and extracted by each of the two methods. The results are given in the following table (A):

TABLE A.

Sample.	METHOD I.			METHOD II.		
	Fat Added. Gram.	Fat Recovered. Gram.	Loss or Gain. Gram.	Fat Added. Gram.	Fat Recovered. Gram.	Loss or Gain. Gram.
Cotton seed oil,	.2180	.2180	0000	.1770	.1760	—,0010
“ “	.2020	.2025	+.0005	.2015	.2010	—,0005
“ “	.2015	.2010	—,0005	.1815	.1810	—,0005
Average,	.2072	.2072	0000	.1867	.1860	—,0007
Butter,	.1775	.1770	—,0005	.1765	.1760	—,0005
“	.1520	.1510	—,0010	.1880	.1870	—,0010
“	.0910	.0910	0000	.1030	.1035	+.0005
Average,	.1402	.1397	—,0005	.1558	.1555	—,0003
Mutton tallow,	.1160	.1165	+.0005	.1470	.1480	+.0010
“ “	.0960	.0960	0000	.0925	.0930	+.0005
“ “	.0970	.0970	0000	.0810	.0815	+.0005
Average,	.1030	.1032	+.0002	.1068	.1075	+.0007
Lard,	.0675	.0670	—,0005	.1415	.1420	+.0005
“	.1345	.1340	—,0005	.0925	.0930	+.0005
“	.2330	.2325	—,0005	.0660	.0660	0000
Average,	.1450	.1445	—,0005	.1000	.1003	+.0003
Beef tallow,	.1100	.1100	0000	.1125	.1120	—,0005
“ “	.1515	.1520	+.0005	.1545	.1540	—,0005
“ “	.0965	.0965	0000	.1335	.1335	0000
Average,	.1193	.1195	+.0002	.1335	.1332	—,0003
Sum of averages,	.7147	.7141	—,0006	.6828	.6825	—,0003

From this table it will be seen that there is no appreciable loss, and that the two methods are about the same when pure fats are being extracted. The different fats employed give about as much range in composition and physical characters as would be expected in the various vegetable fats.

In Table B is given a comparison of the two methods on a variety of samples, which cover fairly well the different classes of substances met with in agricultural analysis. A comparison of the results given in Table B shows that there is a difference in every case, Method I giving the higher result, and in some cases the difference is surprising. This shows that the amount of error which has been introduced into our valuations of feeding stuffs, calculation of digestibility and nutritive ratios is very much more exaggerated and misleading than has been supposed. The results in Table B are the average of triplicate determinations.

TABLE B.

Description of Sample.	I.	II.	Difference Per Cent.
	Per Cent. Fat.	Per Cent. Fat.	
Clover hay, ...	3.51	2.02	1.49
Corn fodder, ...	6.17	2.69	3.48
Corn meal, ...	4.63	4.53	0.10
Cotton seed meal, ...	10.50	9.88	0.62
Dung from digestion experiment on cotton seed meal, ...	5.83	3.83	2.00
Oats hay, ...	4.12	2.57	1.55
Soja bean silage, ...	5.53	4.70	0.83
Sorghum fodder, "Early Orange,"	5.46	2.70	2.76
Sorghum silage, "Amber,"	6.15	3.68	2.47
Tomatoes (dried), ...	10.07	6.48	3.59
Unknown pea, ...	3.44	1.76	1.68
Wheat bran, ...	3.80	3.33	0.47

Having noticed the acidity of the smell of the extract of some of the samples and of ether which was distilled from the extract of some plants, a few tests of the amount of acid in the extracts, soluble in cold water, were made by titrating it with decinormal sodium hydrate, phenolphthalein being used as an indicator. In nearly every case some acid was found in the extract of Method I, reaching over 1 cc. in some cases, there being scarcely a trace from the extract of Method II. The only case in which there was an appreciable amount of acid in the extract of Method II was from the sorghum silage.

From a study of these figures and a close examination of the products obtained by the two methods, it seems that the use of charcoal results in a closer approximation to the truth than any other method in use, though absolute accuracy is not claimed. The following points may be rightly claimed in favor of the use of animal charcoal in the determination of fat (ether extract) in feeding stuffs.

- (1). That the product obtained is nearly pure fat or vegetable oil.
- (2). That the product obtained gives a more correct idea of the physical nature of the fats from various substances.
- (3). That slight quantities of water that may exist in the substance and pass out with the extract will be removed by the charcoal.

(4). That soluble acids of the plant, or acid which may be formed by the continuous distillation of ether, in connection with some constituents of plants, will be partially, if not wholly, removed by the animal charcoal.

(5). That the animal charcoal will partially obviate, if not wholly remove, the difficulty of change in the amount of ether extract (which generally increases) with the aging of the sample.

MD. AGR'L EXPT. STATION, AGR'L COLLEGE, MD., Feb. 8, 1890.

ON THE SOLUBLE CARBOHYDRATES PRESENT IN THE SEEDS OF LEGUMES.

BY W. MAXWELL.

In the analysis of seeds, all that part of their non-nitrogenous constituents which is soluble in water, and which upon boiling with a dilute acid becomes converted into bodies capable of reducing an alkali-copper solution, has been expressed as dextrine. Prof. R. Sachsse,¹ in a study of *Pisum sativum*, estimated that six and a half per cent. of the soluble nitrogen-free extract matters contained in those seeds was composed of dextrine. He stated, moreover, that not any sugars were present. It has further been decided by A. von Asbóth² that the mature seeds of the various representatives of grain do not contain crystallisable sugars; that in all instances where it had been supposed that cane or glucose sugars were present, the preparations of those bodies which had been obtained were consequent products of the methods employed in research.

Although it may be of small moment, in respect of practical or agricultural considerations, whether the conclusions of the given authorities shall be confirmed or not, there is a special physiological interest in trying to determine more precisely the definite characters of those bodies which comprise the soluble carbohydrate-aggregate of leguminous and other seeds.

In the course of a study of the legumes *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, the author³ discovered cane sugar in

¹ Chem. Centralblatt, 1872.

² Bied. Centr., 1888.

³ Landw. Versuchs-Stationen, Bd. 36.

each of those representatives. In addition to saccharose, those examples of seeds contained a white amorphous body which was distinguished chemically from dextrine by the instance that upon boiling with a dilute mineral acid it yielded galactose; and further, when the body was heated with concentrated nitric acid, mucic acid was obtained as the product of oxidation. More recently the seeds of *Phaseolus vulgaris* have been investigated in respect of the presence of soluble carbohydrate bodies, and according to a method and with results which will be more particularised.

The separation of the carbohydrates from the seed material was made by repeatedly extracting with an alcohol of 75 per cent. concentration. The clear extraction was heated to boiling and a saturated solution of strontium hydrate added, and the boiling continued for an hour under a condenser, by which process the carbohydrate bodies were thrown down as saccharates. After some further treatment, the strontium compounds were broken up in aqueous suspension by a current of carbon-dioxide, and the solution evaporated to a syrup. The syrup-residue was extracted by boiling with absolute and 98 per cent. alcohols consecutively, and the extract placed in a desiccator over sulphuric acid. After twenty-four hours a considerable yield of transparent and colorless crystals was obtained, which, upon being recrystallised, appeared in the forms of well-developed monoclinic prisms. The observations of the crystals agreed practically with the crystallographical reading given by Dr. Scholl, Zürich University, of cane-sugar crystals obtained by the author¹ from the seeds of *Faba vulgaris*, and which was as follows:

	Estimated.	Found.
100:110	129° 14'	129° 9'
110:110	78 36	78 30
100:001	103 17	103 14
001:011	139 30	139 30
011:011	99 0	98 0
110:001	127 31	127 19
111: 0	133 59	131 29

After the cane sugar had been separated by extraction with boiling alcohol, a considerable amount of a white-yellow substance was remaining. That residue was taken up in water and

¹ Landw. Versuchs-Stationen, Bd. 36.

treated for the removal of coloring matters, and finally condensed to a very concentrated volume. Upon bringing the solution drop by drop into a beaker containing absolute alcohol, a white, flake-like body separated out, which was brought upon a filter and dried. When the body was boiled with a dilute mineral acid, galactose sugar was obtained, and upon heating with concentrated nitric acid, mucic acid was formed as the oxidation product.

The non-crystallisable carbohydrate which was obtained from the seeds of *Phaseolus vulgaris*, and which was present with some smaller portion of dextrine, seemed to resemble in its appearance and chemical properties the bodies obtained by A. Müntz¹ from *Medicago sativa*, by R. W. Bauer² from *Agar-Agar*, by A. Meyer³ from several caryophyllaceae, by E. Steiger⁴ from *Lupinus luteus*, by A. von Planta⁵ from *Stachia tuberosa*, and by the author⁶ from *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, and which are known as "galactans" or "galactins."

No trace of glucoses was observed in the alcoholic extraction, nor in the aqueous solution after the breaking up of the strontium saccharates. It must be remarked, however, that had any reducing sugars been present, they would have been broken up by the treatment with the strontium hydrate.

When the presence of cane sugar, of galactan, with some portion of dextrine, had been established in the seeds treated of, it appeared desirable to make, at least, an approximate estimation of the amounts of those bodies contained. Before such an estimation could be attempted, it was in the first place necessary to determine the conditions by which a maximum extraction of the soluble non-nitrogenous bodies could be effected. As a first experiment, the material was repeatedly extracted with cold water. In another example the material was extracted with water at boiling temperature, and the starch, which was suspended in the extract, was thrown out with a barium solution; that method, however, gave lower results than the extraction with cold water, indicating that some amount of the soluble carbohydrates had been separated either chemically or mechanically with the starch. A third experiment was made by extracting with water at a temperature of 37°-40° C., at which temperature it was observed that a maximum extraction was obtained, and the solution was free from starch,

¹ Compt. rend. 94.

⁴ Inaugural Dissertation, 1887.

² J. prakt. Chem. 30.

⁵ Landw. Versuchs-Stationen, Bd. 35.

³ Ber. d. chem. Ges. 17.

⁶ Ibid. Bd. 36.

which was shown by the iodine test. It was determined to extract at 38° C., using water at the same temperature for washing out the residue. The extract solution was treated with a very small volume of phosphotungstic acid, before inverting with hydrochloric acid, the latter being conducted according to Sachsse.¹

The estimations of the inversion products were made gravimetrically as given by Allihn,² and are expressed in the following analytical data:

- I. 8.21 grams material yielded = 0.4896 gram sugar.
= 0.440 gram carbohydrates.
= 5.359 per cent.

- II. 10.05 grams material gave = 0.599 gram sugar.
= 0.539 gram carbohydrates.
= 5.362 per cent.

The mean of two given weights of material extracted, and of four determinations of the sugar present in the extractions, indicate that the seeds of *Phaseolus vulgaris* contain soluble carbohydrates to the extent of 5.36 per cent.

A quantitative separation of the cane-sugar, galactan, and dextrine was not attempted. A method which would render anything more than qualitative indications of those several bodies does not at present obtain.

When it is known that those soluble carbohydrates are contained in mature seeds, the question occurs most consequently as to what are the physiological uses of those bodies in relation to the life of the embryo-plant during the state of incipient growth? A preliminary observation was made with some material which had been prepared by the direction of Prof. Goodale, Harvard University, for other germination studies.

The seeds of *Phaseolus vulgaris* were germinated and allowed to develop until the radicle was one and a half centimeters in length, at which stage the growth was suddenly stopped by drying the material, seed and radicle together, at 100° C. An estimation of the soluble carbohydrates contained in the material, composed of the partially exhausted seed and the crudely formed radicle, was made exactly the same as in the example of the mature seed.

¹ Chem. Centralblatt, 1877.

² J. prakt. Chem. 23.

- I. 6.865 grams material gave = 0.258 gram sugar.
 = 0.232 gram carbohydrates.
 = 3.37 per cent.
- II. 6.742 grams material gave = 0.262 gram sugar.
 = 0.235 gram carbohydrates.
 = 3.33 per cent.

When the mean of those estimations, 3.35 per cent., is compared with the amount of those bodies contained in the mature seed, it is found that thirty-two per cent. of the soluble carbohydrates had disappeared, were used up by the embryo-plant in the earliest stage of its development, and during the short time which was necessary for the protrusion of the radicle, and before the plumule had made its appearance.

No observation was made in order to determine which of the soluble carbohydrates had first been absorbed by the plantlet. Only so much is indicated by the given experiment that the soluble carbohydrates present in the seed provide the germ with its first requirement of non-nitrogenous substance, and until the starch has been acted upon by the ferments originated by the movement of the germ and prepared for appropriation.

The observations which have been given are preliminary to a proceeding study of the value and disposition of given bodies during germination.

HARVARD COLLEGE LABORATORY.

REVIEWS AND REPORTS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

III. *Further Notes on the Sulphuric Acid and Alkali Industries.*

Sulphur.—In spite of the nearly complete abandonment of sulphur for acid-making in Europe, the production of the Sicilian deposits has not declined, as is indicated by the following table:

Production and Distribution of Sicilian Sulphur (long tons).

Exported to	1883.	1884.	1885.	1886.	1887.	1888.	1889.
England...	41,788	40,760	33,402	30,236	31,086	37,455	37,633
France. ...	63,602	65,098	58,264	54,280	56,221	53,927	68,632
Italy.....	66,810	56,292	49,415	48,658	46,818	48,436	44,317
America...	96,629	94,929	99,378	98,590	88,593	128,953	111,838
All other countries.	67,563	56,829	74,123	97,691	89,728	86,590	99,592
Total....	336,392	314,058	314,582	329,455	312,446	355,361	362,012

This country has for many years imported more sulphur than any other; the above table shows that more than one-third of the Sicilian product came to America in 1888. In addition to this, constantly increasing quantities of sulphur are imported into this country from Japan, amounting in 1888 to 6332 tons. Practically no sulphur was mined in the United States in 1888, the deposits at Cove Creek, Utah, not having been worked, although they produced 3000 tons in 1887.

Considerable quantities of sulphur, recovered from tank-waste in England by the Chance process, have been sent to this country during the past year, the importations for 1889 amounting to about 1000 tons. The writer is informed by Mr. George Linder, of Boston, the American agent for the Chance company, that contracts have been made for 500 tons per month during the present year. The Chance sulphur is nearly chemically pure, and commands a higher price than the Sicilian crude; its chief use thus far is in making sulphur dioxide for the sulphite process of wood-pulp manufacture. It would seem particularly well suited for gun-powder making, but has not yet been adopted for this purpose.

The refining of sulphur is still chiefly carried on at Marseilles, where there are now six refineries in operation. These works, with five others at various points in the south of France, produce annually about 60,000 tons of refined sulphur, a very large part of which is used to combat diseases of the vine.

Pyrites.—The Spanish and Portuguese mines are producing pyrites in undiminished quantities. More than two million tons were mined in 1887. The importation of pyrites into England shows no falling off, in spite of the precarious condition of the Leblanc-soda process. According to the Board of Trade returns, the quantity of pyrites imported into the United Kingdom during the past six years is as follows:

Importations of pyrites into the United Kingdom (long tons):

1884.	1885.	1886.	1887.	1888.	1889.
563,073	654,521	556,988	597,595	617,232	643,879

This is practically all supplied by three great companies, the Tharsis and Rio Tinto, in Spain, and Mason & Barry, Portugal. The Rio Tinto Co. made efforts some years ago to introduce Spanish pyrites into France and other countries, and to this end established a large plant for the manufacture of Leblanc soda and treatment of pyrites cinders for silver, gold and copper, at Marseilles. These works are still in operation, but owing to the unpromising outlook of the Leblanc process the project of erecting similar works in Belgium, Austria and America has been abandoned. French pyrites, containing no copper, mined at various points along the course of the Rhone, is employed at all the chief alkali works in France.

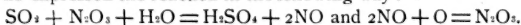
¹ Weldon, J. Soc. Ch. Ind. 1883, p. 4.

In America, the production of pyrites has increased considerably within a few years. In 1888, 54,331 tons of pyrites were mined in the Eastern States, chiefly at the Davis Mines, Franklin Co., Mass. Large quantities of ore are also imported from Canada and Spain. According to W. H. Adams (Manufacturers' Record, Feb., 1890), the mines of Virginia will produce during the present year fully 70,000 tons of pyrites. The same writer estimates the consumption of pyrites for the present year at 250,000 tons. The importations from Canada will probably reach 50,000 tons.

Treatment of Pyrites Residue.—The treatment of the cinders from burnt Spanish pyrites by the Henderson process is carried on in England on an enormous scale, and is constantly increasing. In 1888, 420,415 tons of burnt ore were treated in Great Britain, producing 15,135 tons of copper, 337,500 ounces of silver, and 1918 ounces of gold.

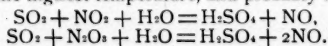
Theory of the Sulphuric Acid Process.—Within the past few years the question of the precise nature of the reactions which take place in the lead-chambers has been fully discussed by Lunge, Raschig, and others, and much light has been thrown on the various stages of the process. An able review of this work has been given by Dr. Hamburger,¹ and need not here be repeated. The chief conclusions reached may, however, be briefly stated.

Lunge,² by a careful study of the gases present in chambers in actual operation, found that nitrogen peroxide (NO_2) is rarely present, and can only exist in practical absence of moisture and sulphur dioxide. Nitrous anhydride, N_2O_3 , is the active agent in the production of sulphuric acid. This view was held by Berzelius, who expressed the reaction in the following way:



Lunge showed that these reactions cannot be correct, since, if true, sulphuric acid whenever formed should be accompanied by a corresponding quantity of nitric oxide; whereas nitrous anhydride only is present in the greater part of the chamber-space. Further, nitric oxide and oxygen do not give nitrous anhydride, as indicated by the second reaction, but yield nitric anhydride or nitric acid according to the absence or presence of water. These observations upset all theories based upon the reduction of nitrogen compounds to nitric oxide. Nevertheless nitric oxide is found to be present to some extent in the first chamber. Lunge considers the material of the "chamber crystals," or nitrosulphonic acid, $\text{SO}_2(\text{OH})\text{NO}_2$, to be an important intermediate product in the synthesis of sulphuric acid. In view of these observations the course of the reaction appears to be as follows:

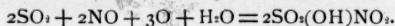
In the first chamber the gases meet in the most concentrated state and at the highest temperature, and probably react thus:



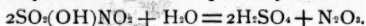
¹ J. Soc. Ch. Ind. 1889, p. 164.

² Chemische Industrie, 1884, p. 5.

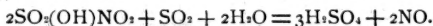
The nitric oxide immediately combines with sulphur dioxide, oxygen and steam to form nitrosulphonic acid :



The nitrosulphonic acid is decomposed by steam :



Or, in the presence of excess of sulphur dioxide and steam, and at a high temperature, the decomposition may take place as follows :



This reaction takes place in the Glover tower, and accounts for the presence of nitric oxide in the first chamber. Lunge explains the loss of nitre in the process by the reduction of part of the nitrogen compounds to lower oxides or free nitrogen, and also the formation of nitrogen peroxide in the last chamber on account of too great excess of nitrous gases and deficiency of sulphur dioxide.

Present Condition of the Alkali Industry.—In spite of the strikingly rapid growth of the ammonia-soda industry, there has been no decline as yet in the production of alkali in Great Britain by the Leblanc process. This is shown by the statistics of the importation of pyrites, given on page 270, and by the following table, compiled from the latest Alkali Inspectors' reports.

Salt decomposed by both processes in the United Kingdom (tons):

	1884.	1885.	1886.	1887.	1888.
Leblanc process,	578,874	598,096	584,323	577,381	590,312
Ammonia-soda process, .	89,759	115,032	137,220	158,636	212,181
Total, .	668,633	713,128	721,543	736,017	802,493

These figures show that in Great Britain the older process is holding its own, though the world's growing demand for alkali is supplied by the increase of the new industry. Weldon showed five years ago that soda-ash can be produced fully one-third cheaper by the ammonia-soda makers; the survival of the Leblanc process is therefore due to the enormous demand for bleaching powder (which has not yet been made economically by any other method), and to the profits gained in the treatment of pyrites-cinders. Another important gain to the Leblanc industry is the success of the Chance process of sulphur recovery, which has now been introduced into most of the leading alkali works of Great Britain and the Continent. The effect of this new source of profit will be shown in the returns for the present year. The Leblanc-alkali makers have lately devoted themselves almost entirely to the manufacture of caustic soda and soda-crystals, for which the older process possesses important advantages over the new.

Outside of England the advance of the ammonia-soda process has been even greater, while the production of the Leblanc works has fallen off in a marked degree. According to the Paris Exposition Circular of the Solvay Co., the world's total production of alkali in 1888, calculated as soda-ash, may be estimated at about 900,000 tons. Of this amount 430,000 tons, or about one-half, was made by the ammonia-soda process at the various Solvay works. The latter have increased their production still further during the past year, so that it may probably be safely said that more alkali is to-day produced by the ammonia process than by that of Leblanc.

There are now ten Solvay works in operation, the location and output of which are as follows:

Belgium (Couillet), ...	17,000 tons.
France (Varangeville-Dombasle), ...	100,000 "
England (Brunner Mond & Co., Northwich), ...	125,000 "
Germany (Wylhen, Bernburg and Sarralbe), ...	100,000 "
Russia (Beresniki and Lissitchansk), ...	17,000 "
United States (Syracuse, N. Y.), ...	60,000 "
Austria (Ebensee, Salzkammergut), ...	11,000 "
	430,000 "

The works at Geddes, near Syracuse, now supply about one-third of the American demand; in addition to the product of these works there was imported from England in 1888 125,135 tons of alkali.

Other modifications of the ammonia-soda process, such as that of Parnell and Simpson (see the writer's second paper on Progress of Industrial Chemistry, this Journal, March, 1889), and the Schloesing process, introduced by Bell Bros., Middlesbrough, England, are worked only on an experimental scale and do not as yet play an important part in the alkali industry.

The Hargreaves Process.—The direct conversion of salt into sulphate of soda by the action of sulphur dioxide and steam has come into increased use during the past few years. There are now five works in England using this process, and also one in Ireland and two in France. During the year 1888 these works produced 43,080 tons of sulphate. The advantages of this method over the ordinary salt-cake process are the avoidance of the cost of making sulphuric acid, and the purity and freedom from iron of the sulphate so obtained. No fuel is found necessary, the heat of the reaction being sufficient after the operation is once started. The disadvantage of the method is the high first cost of the plant. Nearly all the plate-glass now produced in Lancashire is made from Hargreaves sulphate.

Chlorine and Bleaching Powder.—The Weldon-Pechiney process, based upon the decomposition of moist magnesium oxy-

chloride by heat into magnesia, hydrochloric acid and free chlorine, is in successful operation at Salindres, France, and has been introduced on a large scale at the works of Albright & Wilson, at Oldbury, near Birmingham, England. An outline of the process was given in the writer's last paper referred to above. This method accomplishes the final conversion into free chlorine of more than 90 per cent. of the hydrochloric acid employed, while the Weldon process, now universally employed, yields only one-third of the chlorine in a free state. An interesting application of the new process has been made at Szczakowa, Galicia, in the manufacture of chlorine from the waste products of the ammonia-soda industry. The residual calcium chloride is converted into magnesium chloride by treatment with magnesia and carbon dioxide,



(as in the last stage of the old Schaffner & Helbig method of sulphur recovery). The magnesium chloride is treated by the Weldon-Pechiney process for the production of chlorine, and the residual magnesia used over again. This method is a partial solution, at least, of the great problem of the production of chlorine from salt in connection with the Solvay process. The great obstacle to the employment of the Weldon-Pechiney process on a large scale is, however, the dilute condition of the chlorine liberated, which makes it unfit for the manufacture of bleaching powder. At present, the method is employed solely for the production of chlorates, for which it is especially adapted. Until the problem of the manufacture of bleaching powder from this weak chlorine is successfully worked out, it is not to be expected that the process will have an important influence on the alkali industry.

Other methods for the production of chlorine from the ammonia-soda residues appear to be unpromising. The Solvays are making hydrochloric acid on a small scale at the Varangeville works, by heating calcium chloride with silica, but the plan makes no progress and is probably very uneconomical. Mond's method of obtaining ammonia and chlorine by passing ammonium chloride vapor over heated nickel or cobalt oxide is still wholly in the experimental stage, though the inventor promises full success in two years at farthest.

Recovery of Sulphur from Tank-Waste.—The Chance process has been introduced at twenty works in Great Britain, one in Austria, and one in France. It was recently stated by the manager of the St. Gobain Co. (France) that the sulphur so regained is sold at a price equal to three times its cost in the form of pyrites. As stated on page 270, considerable quantities of the Chance sulphur are already being exported to America. An important advantage of the process to English alkali makers consists in its availability for the production of either sulphur or

sulphuric acid. If pyrites is cheap, sulphur is manufactured and exported to America and other countries; if pyrites is expensive, the hydrogen sulphide produced from the tank-waste is simply burned to sulphur dioxide and used over again for making acid. It is interesting to reflect that the sulphur imported into England in enormous quantities in the form of pyrites now no longer becomes a source of nuisance in the shape of tank-waste, but passes through the various stages of sulphur dioxide, acid, sulphate of soda, tank-waste and hydrogen sulphide, and finally appears at the end of the process as beautiful crystalline sulphur, a product of high commercial value.

SPENCER B. NEWBURY.

THE USES OF HYDROGEN DIOXIDE IN QUANTITATIVE ANALYSIS, AND THE IMPORTANT METHODS FOR DETERMINING HYDROGEN DIOXIDE.

The more important applications of hydrogen dioxide for quantitative purposes are given below.

Classen and Bauer¹ found that hydrogen dioxide can be used advantageously in the determination of hydrochloric, hydrobromic and hydriodic acids in the presence of sulphuretted hydrogen. The latter is oxidised to sulphuric acid, and the chlorine, bromine and iodine are then determined in the usual manner.

The oxidation of sulphur to sulphuric acid by hydrogen dioxide is also employed to separate arsenic, antimony, zinc, copper and cobalt from the sulphur in their sulphides.

The sulphur can be liberated as sulphuretted hydrogen and oxidised by hydrogen dioxide. They employed this method in the determination of antimony trisulphide, antimony pentasulphide, tin, cadmium, and iron sulphides. It was found that hydrogen dioxide will also readily oxidise sulphur dioxide. This reaction is therefore employed to oxidise barium and sodium sulphites and sodium hyposulphite to sulphates.

P. Ebell² determined lead dioxide by hydrogen dioxide in two ways. He used a known amount of the hydrogen dioxide, allowed it to decompose the lead dioxide, and then titrated the excess with potassium permanganate. He also effected the same decomposition, and measured the volume of the resulting gas. He recommends the former method. The latter method gave results which were too low as compared with those obtained by other methods.

G. Lunge³ described a method for determining potassium permanganate and manganese dioxide by means of an excess of hydrogen dioxide and sulphuric acid. The oxygen evolved was collected and measured, half coming from the manganese dioxide and half from the hydrogen dioxide.

The same author⁴ proposed later a method for determining the

¹ Ber. d. deutsch. chem. Gesell. **16**, 1061.

² Ber. d. deutsch. chem. Gesell. **18**, 1872.

³ Rep. anal. Chem. **6**, 141-43.

⁴ Ibid. **19**, 868.

available chlorine in bleaching powder by means of an excess of hydrogen dioxide, half of the oxygen evolved coming from the bleaching powder and half from the dioxide. But the volume of the oxygen set free is just equal to the total volume of the available chlorine in the bleaching powder.

A. Carnot¹ determined chromic acid by hydrogen dioxide. The slightly acidulated bichromate solution was titrated with very dilute hydrogen dioxide, which was then standardised by means of pure bichromate. The end of the titration is shown by the absence of the blue color when the dioxide is dropped into the chromic acid solution.

G. Lunge² recently recommended the slightly modified nitrometer for standardising potassium permanganate, and for determining bleaching powder and manganese dioxide by hydrogen dioxide and sulphuric acid.

Some of the above decompositions have been employed for the determination of the dioxide itself. These and other important methods for determining hydrogen dioxide will be briefly considered.

Barium dioxide was determined by Brodie³ by treating it with hydrochloric or acetic acid in the presence of finely divided platinum or of animal charcoal, which decomposes the hydrogen dioxide catalytically. The apparatus, including the materials used, was weighed and the acid admitted to the barium dioxide. Decomposition having taken place, the apparatus was again weighed. The loss in weight equals the weight of the oxygen evolved.

In water solution, hydrogen dioxide has been determined by Schönbein.⁴ He acidified the solution with sulphuric acid in order to secure the complete reduction of the permanganate. The solution thus acidified was titrated with standard potassium permanganate until the first traces of color appeared.

Another application of this same reaction has been proposed by F. Hamel.⁵ He treated the dioxide with a permanganate solution, collected and measured the oxygen evolved. At the same time he standardised his permanganate solution for further use.

Instead of potassium permanganate, A. Riche⁶ employed manganese dioxide and sulphuric acid for determining hydrogen dioxide. The oxygen liberated was collected and measured. Lead dioxide is also used for the same purpose.

A method has been proposed by A. Houzeau⁷ which is based on the following reaction in acid solution: $\text{H}_2\text{O}_2 + 2\text{KI} = 2\text{KOH} + 2\text{I}$. A measured amount of standard acid was introduced into the neutral solution of the hydrogen dioxide to be determined. A small excess of potassium iodide was then

¹ Compt. rend. 107, 948.

² Phil. Trans. 1850, 2, 779.

³ Compt. rend. 76, 1023.

⁴ Jour. Soc. Chem. Indst., January, 1890, 21.

⁵ Jour. für prakt. Chem. 79, 78.

⁶ Jour. pharm. Chim. [6] 13, 249-56.

⁷ Compt. rend. 66, 44.

added. The iodine liberated was boiled off and the excess of acid titrated with standard alkali.

Bertrand¹ used the above reaction to determine barium dioxide and hydrogen dioxide. Instead of driving off the iodine and titrating the excess of acid, he titrated the liberated iodine with a standard solution of sodium hyposulphite.

For the detection and determination of small quantities of hydrogen dioxide, Schöne² makes use of the decomposition of potassium iodide by the dioxide in neutral solution, and the detection of the free iodine by means of starch paste. He states that this method will detect 0.00008 gram in a liter. When there is more dioxide present than 0.001 gram in a liter, the method is not accurate, since the color does not change in the same ratio as the substance. A milligram and two-tenths to a liter give about the same color as a gram. The minimum limit of accuracy is 0.00008 gram, and the maximum 0.001 gram of the dioxide to the liter.

G. Lunge³ reversed his method for determining bleaching powder by hydrogen dioxide, and determined the dioxide by means of an excess of bleaching powder. The volume of the oxygen set free was measured, half coming from the bleaching powder, half from the dioxide.

Potassium bichromate has been used by Wilfart⁴ for an approximate determination of hydrogen dioxide. The dioxide was treated with dichromate and sulphuric acid, and the liberated oxygen measured.

A. Carnot⁵ titrated the dioxide with a standard solution of potassium bichromate in the presence of a little hydrochloric or sulphuric acid. Carnot states that this method is not as reliable as the permanganate method.

Attention is called to a piece of apparatus recommended by Maurice de Thierry⁶ for determining hydrogen dioxide.

Some work which I have done in this laboratory shows that the applications of hydrogen dioxide to quantitative analysis can be extended by the use of nitric acid instead of sulphuric. This works more satisfactorily where the formation of insoluble sulphates is involved. Thus, minium and lead peroxide yield thoroughly satisfactory results when treated with nitric acid and hydrogen peroxide. The commercial hydrogen dioxide should in all cases be diluted three or four times to prevent decomposition on standing.

For the determination of minium, an excess of the diluted dioxide and dilute nitric acid are placed in a 200 cc. Erlenmeyer flask. About a gram of minium is weighed in a weighing tube of convenient size, which is then placed upright in the flask. The flask is connected with a Hempel's burette or a Lunge nitrometer.

¹ Bull. Soc. Chim. d. Paris **33**, 148.

² Ber. d. deutsch. chem. Ges. **19**, 868.

³ Compt. rend. **107**, 948.

⁴ Zeit. für anal. Chem. **18**, 154.

⁵ Zeits. für anal. Chem. **1888**, 417.

⁶ Jour. pharm. Chim. [5] **12**, 501-2.

The gas volume, after adjustment of pressure, is read. The weighing tube containing the minium is then overturned into the mixture of nitric acid and hydrogen dioxide. In a few minutes the decomposition is complete. The increase in volume is ascertained and reduced to standard conditions of temperature and pressure. Half of the oxygen comes from the minium and half from the hydrogen dioxide. The water in the burette should be made slightly alkaline with sodium or potassium hydroxide, to remove any traces of carbon dioxide which may come from the action of nitric acid on impurities in the minium. The results obtained, expressed in percentages of oxygen, were :

Oxygen.

2.40 per cent.

2.39

2.36

Average, 2.38 +

To test the above results, portions of the same specimen of minium were heated in a vacuum, the oxygen pumped away as rapidly as it was set free, and measured after removal of carbon dioxide. Under these conditions the minium passed completely into lead oxide. The results were :

Oxygen.

2.37 per cent.

2.36

2.36

Average, 2.36 +

We attempted to determine the oxygen in the same specimen of minium by heating it in hard glass tubes attached to a Hempel's burette and measuring the oxygen evolved. Platinum gauze was placed in the tube to facilitate the distribution of heat. The results, expressed in percentages of oxygen, were :

Oxygen.

2.19 per cent.

2.21

2.22

2.26

2.20

Average, 2.21 +

As will be seen, the results are too low. This is to be attributed to a partial recombination of the lead oxide and oxygen during cooling.

The method¹ sometimes employed for determining lead dioxide

¹ Zeits. für anal. Chem. 14, 348.

by heating in the air and ascertaining the loss in weight is subject to the same source of error.

The determination of lead dioxide was carried out in all respects like that of minium. The specimen should be finely pulverised, and a half gram or less used in a determination. The results with hydrogen peroxide and nitric acid, expressed in percentages of oxygen evolved, were:

Oxygen.
5.43 per cent.
5.43
5.42

Average, 5.42 +

Determinations of the same specimen by heating in a vacuum were carried out as in the former case. More carbon dioxide was found here than in the minium. .3 per cent. of carbon dioxide was removed from the oxygen. The results, expressed in percentages of oxygen, were:

Oxygen.
5.45 per cent.
5.43

Average, 5.44

The determination of manganese dioxide by hydrogen dioxide and sulphuric acid has been made by Lunge as above mentioned. But we find that nitric acid is preferable, as will appear below.

A specimen of manganese dioxide was ground and dried. Two determinations were made by Lunge's method, with the following results:

Oxygen.
13.13 per cent.
13.14

Average, 13.13 +

Two determinations of oxygen in the same specimen, made with the use of dilute nitric instead of sulphuric acid, gave:

Oxygen.
13.17 per cent.
13.24

Average, 13.20 +

The slightly higher results in the second case are perhaps due to the presence of ferrous iron in the ore, which was oxidised by the nitric acid, and loss in available oxygen avoided. To test this we added equal amounts of a ferrous salt to weighed portions of the manganese dioxide, and determined the oxygen by sulphuric and nitric acids respectively. The results obtained when sulphuric

acid was used were slightly lower, while when nitric acid was employed they were practically constant. This tends to confirm the above idea.

That hydrogen dioxide can be determined by minium and nitric acid, or lead dioxide and nitric acid, will be seen from the following results. The specimen was first determined by calcium hypochlorite. The results are expressed in liters of oxygen obtained from one liter of hydrogen dioxide.

Results when calcium hypochlorite was used:

	Oxygen.
	5.890
	5.890
	5.880
Average,	5.8866 +

Results when minium and nitric acid were employed:

	Oxygen.
	5.900
	5.910
	5.910
Average,	5.9066 +

Results from the decomposition by means of lead dioxide and nitric acid:

	Oxygen.
	5.910
	5.900
	5.910
Average,	5.9066 +

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A DICTIONARY OF APPLIED CHEMISTRY. By T. E. THORPE, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 1. London and New York: Longmans, Green & Co., 1890. Price of Vol. 1, \$15.00.

The following extract from the preface of this work will explain its object:

"This work is essentially a dictionary of chemistry in its applications to the arts and manufactures; hence it deals but sparingly with the purely scientific aspects of chemistry, unless these have some direct and immediate bearing upon the business of the technologist. For all such matters reference is made to the new edition of 'Watts' Dictionary of Chemistry,' by Dr. Forster Morley and Mr. Pattison Muir, to which, indeed, the present work

may be said to be complementary. In order to facilitate such reference the general plan and method of arrangement of the two dictionaries are similar, and the nomenclature and notation adopted are practically identical." "Although the two works are, in a broad general sense, complementary, it is practically impossible to avoid a certain amount of overlapping, and therefore a certain degree of independence. Hence in the present work the chemical history of a product of technical importance, so far as it is known, has often been completed, although its derivatives have, at present, no applications in the arts. Moreover, such subjects as the atmosphere, water, fermentation, the chemistry of the hydrocarbons, the vegeto-alkaloids, glucosides, etc., etc., all of which are dealt with in the other work, find also a place in this dictionary by reason of their relations to technology or to medicine and sanitation. In all cases, however, these subjects are treated from the standpoint of practical application."

The first volume ends with Dysodil. Among the longer and more important articles contained in it are: Disinfectants, by A. H. Allen; Copper, by E. J. Ball; Butter, by James Bell; Acidimetry and Alkalimetry and Analysis, by C. H. Bothamley; Cellulose, by C. F. Cross; Balance and Cyanides, by W. Dittmar; Candles, by Leopold Field; Aniline, Aniline Black, Aniline Blue, Aniline Salt, Benzene and its Homologues, by R. J. Friswell; Anti-corrosive Compositions and Methods, and Anti-fouling Compositions, by J. B. Hanway; Cements, by W. N. Hartley; Brewing, by John Heron; Bleaching, Dyeing, Detection of Colors in Dyed Fabrics, by J. J. Hummel; Benzaldehyde, Benzoic Acid, Cinnamic Acid, Cymenes, Diphenyl, etc., by F. R. Japp; Ammonia, Bromine, and Chlorine, by G. Lunge; Azo-coloring Matters, by Raphael Meldola; Animal Charcoal, by J. A. R. and B. E. R. Newlands; Creosote, by B. Nickels; Alizarin and Allied Coloring Matters, by W. H. Perkin, Jun.; Alloys and Assaying, by W. C. Roberts-Austen; Albuminoids, by H. H. Robinson; Agate, Corundum, Diamond, etc., by F. W. Rudler; Balsams, Camphor, Chloroform, etc., by Alfred Senier; Carbohydrates, by Cornelius O'Sullivan; Alcohol, by G. N. Stoker; Barium, Calcium, by A. E. Tutton; Cereals, Citric Acid, by R. Warington; Azines, by Otto N. Witt; Aurine, by W. P. Wynne; Distillation, by Sydney Young.

It is evident from this list that the editor has selected his contributors with care, and that, so far as possible, the articles have been written by men who are specially fitted to write on the subjects assigned to them. We may fairly assume that Professor Lunge gives us reliable information on the subjects of ammonia and bromine and chlorine; and the same may be said of Professor Roberts-Austen and Assaying, Professor Meldola and Azo-coloring Matters, Dr. Witt and Azines, etc. It would almost be an impertinence to question their statements.

As examples of thoroughness and clearness the articles on Analysis, Bleaching, Brewing, Carbon, Cellulose, Cement, Chlorine, Cyanides, Disinfectants, Distillation, and Dyeing are worthy of special mention.

The chemist, whether engaged in technical work or not, will find the book of great value, and he will hardly look for information without finding it. There is, in fact, no other book in English or in any other language which gives as fresh and as reliable information on subjects connected with industrial chemistry.

NOTES.

The Chemical Examination of Baking Powders.

Bulletin No. 13 from the Chemical Division of the U. S. Agricultural Department discusses the results of recent investigations into the composition and relative values of the common baking powders.

Nothing has been invented which equals the action of yeast for aeration of bread, since it introduces no foreign materials, but makes the required carbon dioxide from the carbohydrates already existing in the dough. Another method which leaves no residues in the bread is that invented by Dr. Dauglish, in which the dough is worked under pressure with water charged to saturation with carbon dioxide. On relieving the pressure the dough rises at once. This method has the advantage of being speedy, but bread so made is rather insipid. It is used to some extent in the larger cities of Great Britain.

The demand for a quick-rising dough has been met in this country by the various forms of baking powder, and their use has grown to very large proportions. It is estimated that from fifty to seventy-five millions of pounds are consumed annually in the United States, the smaller number representing a value of twenty-five millions of dollars. Many suppose that all the constituents of the powders are driven off in the process of baking, and this opinion is encouraged by the manufacturers; it is, of course, untrue in nearly all cases, and the character of the residues, in view of the enormous consumption of bread containing them, becomes of very great importance.

Baking powders consist essentially of a carbonate or bicarbonate to supply the carbonic acid gas, and an acid which can liberate it, together with some inert substance, usually starch, to prevent chemical action on standing, due to too close contact of the active

ingredients and too rapid evolution of gas when the powder is used. The different powders in use may be conveniently classified as follows by their acid constituents, bicarbonate of soda being almost universally employed as the alkaline ingredient:

(1) *Tartrate powders*, in which the acid part is taken by tartaric acid or, more commonly, its acid potassium salt. Of this class the report says, "the residue is probably the least objectionable of any of those left by baking powders." This residue is simply potassium-sodium tartrate or Rochelle salt. The amount contained in a loaf of bread made with tartrate powder is about equal to the quantity contained in a Seidlitz powder. Free tartaric acid leaves less residue, but it is more difficult to regulate the evolution of gas when the powders are made from it, and they are more likely to deteriorate on standing.

(2) *Phosphate powders*. Monocalcium phosphate is here employed to liberate the carbon dioxide. It is made by the action of sulphuric acid on bone, and nearly always contains some calcium sulphate as impurity. The residues from the phosphate powders consist of the insoluble phosphates of calcium and sodium. It may be said in general that these residues are not more objectionable, though larger in quantity, than those from the tartrate powders.

(3) *Alum powders*. The gas is set free by the action of either potassium or ammonium alum, no distinction being made commercially between the two. The residues from such powders contain hydrate of aluminum, sodium sulphate, and either potassium or ammonium sulphate, according to the alum employed; very commonly both are present. There is considerable doubt as to the effect of the ammonium salt on the human system. Professor Cornwall, of New Jersey, calls attention to the irritating effects of various other ammonium salts, and thinks careful examination of the action of the sulphate is urgently needed. Tartaric acid or acid calcium phosphate is often added to alum powders with the intention of causing more rapid evolution of gas at first. The former mixture is objectionable, as the aluminum is liable to be retained in soluble form, as the tartrate, instead of being changed to the insoluble hydrate. The mixture of the acid phosphate with the alum powder, on the other hand, is an improvement, since aluminum phosphate is still less soluble than the hydrate. The "alum question" has been much discussed, and, from all the evidence obtainable, the following conclusions are drawn:

(a) That form of alum powder in which sufficient phosphate is added to combine with all the aluminum present is a better form, and less apt to bring alum into the system than where alum alone is used.

(b) It must be expected that small quantities, at least, of alum will be absorbed by the digestive fluids when any form of powder containing it is used.

(c) Whether the absorption of small quantities of alum into the human system would be productive of serious effects is still an open question, and one that careful physiological experiment alone can decide.

In general, it may be said that of the three classes of powders, a tartrate powder gives the lowest percentage of carbon dioxide in proportion to the weight of chemicals used, together with least weight of residue; and a straight alum powder gives the highest proportion of gas and greatest weight of residue.

Ammonium carbonate is sometimes used as a baking powder. Being volatile at baking temperature, no acid is required. If there were certainty of driving off all of it in baking there could be no objection to its use; but, since it acts as a corrosive poison when taken in considerable quantities, great care should be exercised when it is employed.

The report suggests that with a little care, baking powders could be made at home at much less cost than the market price. It recommends as a permanent powder, easily made and without specially drying the ingredients, the following proportions, intimately mixed:

Cream of tartar,		8 oz.
Baking soda,		4 "
Corn starch,		4 "

If too little starch is used, baking powders deteriorate when kept; if too much, the powder is weakened.

Curiously enough, no such thing is recognized in legislation as adulteration of baking powder unless some substance is included which can be shown to be injurious to health. Merchants can be prosecuted for selling impure cream of tartar, but if it is mixed with other chemicals and sold as baking powder no law is violated. Yet it can hardly be denied that some safeguard is needed with a substance so widely and so constantly used. The report recommends that manufacturers be required to use a label giving approximately the composition of the powder sold. "This is in harmony also with modern ideas in regard to legal regulation of the sale of food-stuffs, the tendency nowadays being to allow the sale of cheap substitutes for any article of food so long as they are not injurious to health, but to make all possible provision to insure that the purchaser shall know exactly what he is getting." Attention may be called to analogous regulations concerning fertilizers, and it is shown that all reasons for such requirements in this case apply with equal or greater force when applied to the subject of baking powders.

J. H. HOLMES.

Perseite, a Heptacid Alcohol.

M. Maquenne has recently made known¹ the results of his investigation of the subject of the composition of perseite, a sub-

¹ Ann. chim. Phys. [6] 19, 5 (January, 1890).

stance found in the leaves, berries, etc., of the *Laurus Persea*. Discovered in 1831 by Avequin, who supposed it identical with mannite, as did also Melsens, who made the first analysis of the substance, perseite was regarded by Müntz and Mercano¹ as isomeric with mannite, having, however, a higher melting point, possessing no rotatory power, and differing markedly also from that alcohol in crystalline form. From dulcite, which melts at the same temperature, it is to be distinguished by its lesser crystallising power, and by the fact that, like mannite, its aqueous solution becomes dextro-rotatory on addition of borax. Perseite is very soluble in hot water; on cooling, the solution deposits the greater part of the substance in crystalline condition. It is almost insoluble in alcohol.

M. Maquenne now finds that perseite is not isomeric with mannite, but is a *heptacid* alcohol derived from heptane. A mere determination of the percentage of carbon and hydrogen in perseite would not be likely to lead to any satisfactory conclusion with regard to the composition of the substance, since the percentages of carbon in compounds represented by the formulae $C_7H_8(OH)_6$ and $C_7H_8(OH)_7$ differ by only six-hundredths; of oxygen by but eight-hundredths of one per cent. Even in the proportions of hydrogen the difference amounts to only fifteen-hundredths of one per cent. A careful study, therefore, of several derivatives was necessary in order to establish the composition of this alcohol. It should be mentioned in passing that a determination of the molecular weight by Raoult's method did not yield satisfactory results.

In the presence of zinc chloride, acetic acid and perseite react upon each other, giving rise to the formation of a heptacetate, $C_7H_8(O.CO.CH_3)_7$. The analysis of this compound gave figures agreeing almost exactly with those required for a substance of the formula given above, and, further, by saponification by means of baryta and determination of the barium acetate formed, the proportion of acetic acid in the heptacetate was shown to be that expressed by the formula. A heptabutyrate, $C_7H_8(O.CO.C_2H_5)_7$, was also made and analysed by the same methods. Fuming nitric acid forms with perseite a heptanitate, $C_7H_8(NO_3)_7$, which resembles nitromannite and nitroinosite, but is more stable. A compound with benzoic aldehyde was prepared and shown to have the composition expressed by the formula $C_7H_8O_7(CH.C_6H_5)_7$, where four hydrogen atoms belonging to the alcoholic hydroxyl groups are replaced by the two bivalent groups $(CH.C_6H_5)$.

By heating with hydriodic acid, perseite is converted chiefly into two products: a hydrocarbon of the formula C_7H_{12} , and an iodide of heptane, $C_7H_{15}I$. The hydrocarbon was carefully examined and was found to possess none of the characteristic properties of the hydrocarbons of the acetylene series or of the di-ethylene

¹ Ann. chim. Phys. [6] 3, 270 (1884).

series. It does not combine with the halogens or with the halogen acids to form corresponding derivatives of heptane; the molecule is bivalent, and the products of the action of these reagents are substances whose composition is represented by the formulae $C_7H_{13}Cl$, $C_7H_{13}I$, $C_7H_{12}ClBr$, $C_7H_{12}Br_2$. The derivatives and the hydrocarbon itself show a strong tendency to polymerise. These observations led M. Maquenne to the conclusion that the hydrocarbon must be related to the terpenes, and, indeed, he was able to extract from turpentine a "heptene" which proved to be identical with that formed from perseite. Finally, there was nothing in the reactions of perseite to lead one to the conclusion that the substance is either an aldehyde or a ketone.

W. W. RANDALL.

*Density, Color and Spectrum of Fluorine.*¹

In these new experiments on fluorine, Moissan has prepared the gas in much larger quantity and in a greater state of purity, and has determined some of its physical constants. The method of preparation is identical with that already described,² the apparatus being somewhat larger and the amount of hydrofluoric acid decomposed being greater. The method of purification consisted in passing the fluorine evolved through a platinum spiral cooled down to -50° in a bath of methyl chloride, and then over fragments of sodium fluoride contained in platinum tubes. By this method fluorine entirely free from hydrofluoric acid was obtained. By means of a special platinum flask resembling those used by Berthelot to determine specific heat of liquids and by Charcel to determine density, Moissan found the density of fluorine to be 1.265, the theoretical density being a little higher, viz. 1.316.

Fluorine, on account of its properties and atomic weight, belongs naturally at the head of the chlorine family of elements (F, Cl, Br and I). As all the elements of this family in the gaseous state are colored, and, moreover, the intensity of the color diminishes gradually from iodine to chlorine, it was important to determine whether fluorine possesses any special color. In the previous paper fluorine has been described as a colorless gas, and when thin layers are looked at it apparently has no color. When, however, the gas is inclosed in platinum tubes from a half to a meter in length and closed by plates of transparent fluorspar, a decided color is noticed when a white background is looked at. With a depth of half a meter fluorine is plainly seen to possess a greenish-yellow color, much fainter than that of chlorine seen under the same depth, and, moreover, differing from chlorine in that the shade approaches more towards yellow. Examined by means of the spectroscope under a depth of a meter, fluorine does not show any absorption bands.

¹ C. R. 109, 861; 937.

² This Journal 8, 445.

When a small quantity of water is introduced into the platinum tube the water is decomposed, giving hydrofluoric acid and ozone. This last gas is produced in such a state of concentration that the whole tube takes a deep indigo-blue tint. After a few minutes, owing to the temperature of the laboratory, the ozone is destroyed, the blue tint becomes fainter and fainter and finally colorless. This is the first experiment in which ozone has been produced so concentrated at ordinary temperatures.

The spectrum of gaseous fluorine was determined by Moissan to consist of thirteen lines in the red portion of the spectrum. Five of these agree very well with those already determined by Salet, by comparing the spectra of the chloride and fluoride of silicon.

W. R. ORNDORFF.

Celebration of the Twenty-fifth Anniversary of Kekulé's Benzene Theory.¹

The German Chemical Society arranged a banquet on the 11th of March in honor of Prof. August Kekulé, it being twenty-five years since Kekulé published his theory of the structure of benzene. Beside the chemists resident in Berlin, many other guests were present, including some of the most noted chemists in Germany, those prominent in industrial chemistry as well as those known as teachers; foreign chemical societies, the German government, and the city of Berlin sending representatives.

Before the dinner there was a meeting in the hall of the Rathaus. The president of the society, Prof. A. W. v. Hofmann, greeted the guests in an interesting speech; he noted that this was not the first time chemical discovery had been thus celebrated; he recalled the 100th anniversary of the discovery of oxygen by Priestley, celebrated in America in 1874, and the 50th anniversary of Wöhler's synthesis of urea, celebrated at Göttingen in 1878. It was a feature of the banquet to-day that the man whose theories they celebrated was present and could hear of the importance to which his theory had helped to raise chemical industry. The speaker referred to the time when illuminating gas compressed in iron cylinders was brought to the houses of the consumers, and it was found that the gas partly lost its illuminating power by standing in the cylinders. Faraday showed in 1825 that this was owing to the separation of a liquid—benzene—from the gas. The speaker showed the guests a sealed glass tube containing a few drops of benzene, which Faraday had given him with the advice to keep this very volatile liquid sealed up to prevent evaporation. No one could have foreseen that after a few decades the same liquid would be isolated in quantities of millions of kilograms.

Prof. v. Hofmann closed by introducing Kekulé's oldest pupil, Prof. A. v. Baeyer.

¹ Prepared by E. Renouf from an account given in the *Chemiker-Zeitung* for March 15th, 1890.

Prof. v. Baeyer took as subject for his remarks Kekulé's benzene theory. He showed how the brilliant theories of Kekulé step by step had opened the path to our present views of the structure of chemical compounds; the foundations for the new views were given by his paper on the tetravalence of carbon, published in 1858, and by the illustrative model which he used, representing the atom of carbon as a black ball in the center of a tetrahedron, and to represent its power of union, four rods reaching from the black ball to the points of the tetrahedron, the rods ending in four white balls representing atoms of hydrogen. The paper on the benzene theory was published January 27th, 1865, in the *Journal of the Société de Chimie at Paris*, and on the 26th of February appeared in German in *Liebig's Annalen*. The speaker discussed the opposing theories of the structure of benzene, brought up the objections to the prism theory and to the diagonal nucleus, and claimed that the clearest expression of the structure of aromatic compounds was still Kekulé's benzene ring. Doubtless science would not remain content with this, but would strive to build the structure further; but the point of special significance for the celebration of the day was that the theories of Kekulé had for twenty-five years stood the test of time, and to-day still pointed out the direction of further labor on the building of the structure theory.

Speakers from foreign societies and from the chemical industry followed; then Kekulé spoke, thanking for the honors shown him. Referring to his early studies, he said his father had trained him as an architect, and that he had drawn and planned industriously till he took up the study of chemistry.

Two circumstances had helped him in building up his theories: first, that as a pupil of Dalton and of Liebig, and indeed of all the great chemists of the time, he had belonged to no one special chemical school of thought; and, second, that as a consequence of his architectural training he always strove in his thoughts for a material representation of his ideas of structure. While in London, his mind filled with these subjects, the picture of the union of the atoms in benzene appeared to him in a dream, and on waking he jotted down the principal points of the structure theory, which he then carefully studied and worked out, publishing it eight months later.

After three cheers for Kekulé the guests then went to the dinner at the Hotel Kaiserhof.